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ANY OTHER BUSINESS

Definition and measurement of Black Carbon in international shipping

Submitted by the Institute of Marine Engineering, Science and Technology (IMarEST)

SUMMARY

Executive summary:	This document proposes a definition of Black Carbon, identifies potential measurement methods, offers evaluation criteria to compare measurement techniques, and suggests an appropriate measurement method for international shipping, based on expert guidance and scientific review. The information provided contributes to the current discussions on Black Carbon by identifying the state of the art for its definition and measurement.
Strategic direction:	7.3
High-level action:	7.3.2
Planned output:	7.3.2.1
Action to be taken:	Paragraph 27
Related documents:	MEPC 62/4/10, MEPC 62/4/16 and MEPC 62/4/18

Background

1 During its sixty-second session, the Marine Environment Protection Committee adopted a work plan to address the impact on the Arctic of emissions of Black Carbon from international shipping and instructed the Sub-Committee on Bulk Liquids and Gases (BLG) to: develop a definition for Black Carbon emissions from international shipping; consider measurement methods for Black Carbon, and to identify the most appropriate method for measuring Black Carbon emissions from international shipping; investigate appropriate control measures to reduce the impacts of Black Carbon emissions from international shipping in the Arctic; and submit a final report to MEPC 65 (in 2014).

2 The International Council on Clean Transportation (ICCT), in cooperation with the Institute of Marine Engineering, Science and Technology (IMarEST), conducted an in-depth review of Black Carbon measurement science with the support of international experts in the field. The primary purpose of this document is to address the first two tasks assigned to this Sub-Committee and to provide responses using the best available scientific information.

Definition of Black Carbon emissions from international shipping

3 Carbon-based liquid fuels are the dominant energy source used to power international shipping. Complete combustion of these fuels requires thorough mixing with oxygen at sustained high temperatures in the engine cylinder. In ideal combustion, nearly all the carbon in the fuel would be converted to carbon dioxide.

4 Marine fuels contain heavy oils, ash, and sulphur compounds that limit vaporization and mixing with oxygen. This limits complete combustion of carbon, which leaves some fraction to be emitted as flame-generated carbon particles.

5 Flame-generated carbon is dominated at the molecular level by sp^2-bonds found in graphitic carbon, sp^3-bonds, hydrogen and oxygen. It contains more than 80% carbon by mass, and when emitted forms aggregates of spherules between 20 and 50 nm in aerodynamic diameter. This material contains loosely held electrons whose energy levels are closely spaced, enabling the absorption of electromagnetic radiation across a wide spectrum. This property leads to particles that are strongly light-absorbing and contribute to the positive radiative forcing that causes climate change.

6 Strongly light-absorbing particles constitute an undefined fraction of the total particulate matter emitted by marine vessels. The remaining fraction includes non-absorbing or weakly absorbing carbonaceous particles, solid non-combustible material such as metals, and secondary particulates formed from oxidized sulphur.

7 The light-absorbing properties of carbonaceous particles depend on composition (mixture with other chemicals, especially organic compounds), shape, size distribution, and wavelength. The relationship between light absorption and physical properties (termed the "mass absorption efficiency") varies by engine, fuel, and operating conditions. Recent research by international experts recommends a mass absorption efficiency of 5 m^2/g for light-absorbing carbon from all sources[1].

8 Light-absorbing carbon has been given other names in the climate science community. In climate research, the term "Black Carbon" is used to refer to carbonaceous aerosols that strongly absorb light across a wide spectrum of visible wavelengths with an inverse dependence on the visible wavelength (λ) of light[2]. "Soot" is a term used in combustion aerosol research to refer to all combustion-generated carbon; however, the IPCC uses "soot" specifically to refer to light-absorbing combustion-generated aerosols. Elemental carbon is defined as carbonaceous material that does not oxidize below a temperature threshold around 350°C[3]. All elemental carbon is strongly light-absorbing, but since light absorption is determined by more than elemental carbon content (including morphology, mixing state, and size distribution), not all light-absorbing carbon can be defined as elemental carbon.

9 Based on this discussion, we propose the following definition for Black Carbon:

.1 Black Carbon (BC) is strongly light-absorbing carbonaceous material emitted as solid particulate matter created through incomplete combustion of carbon-based fuels. BC contains more than 80% carbon by mass, a

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1 Personal communication with Dr. Tami Bond, University of Illinois. 8 November 2011.

2 See Bergstrom R.W., Pilewskie P., Russell P.B., Redemann J., Bond T.C., Quinn P.K., *et al*. (2007) Spectral absorption properties of atmospheric aerosols. *Atmos. Chem. Phys.* 7:5937–43.

3 See Cachier, H., Brémond, M.-P., and Buat-Ménard, P. (1989). Thermal Separation of Soot Carbon, *Aerosol Sci. Technol.* 10:358–364.

high fraction of which is sp^2-bonded carbon, and when emitted forms aggregates of primary spherules between 20 and 50 nm in aerodynamic diameter. BC absorbs solar radiation across all visible wavelengths and freshly emitted BC has a mass absorption efficiency of $5m^2/g$ at the mid-visible wavelength of 550 nm. The strength of this light absorption varies with the composition, shape, size distribution, and mixing state of the particle.

Techniques for measuring BC emissions from international shipping

10 The goal of measurement in the context of international shipping is to quantify the mass and light absorption of BC emissions, to develop emission inventories and to inform modelling exercises necessary to evaluate effects on human health and the environment.

11 Instruments are capable of speciating particle mass by chemical or physical properties. However, equating these properties to light absorption requires judgments about the physical nature of light-absorbing particles. It also requires assumptions regarding the relationship between particle mass and light absorption.

12 Instruments are capable of directly measuring light absorption, which is the relevant property of BC. But these instruments are not capable of subsequently measuring the mass of particles identified as being strongly light-absorbing. An assumption of the mass of light-absorbing particles is necessary to complete this measurement.

13 Light absorption and particle mass are related by an assumption of mass absorption efficiency (m^2/g). This value can be specific to a wavelength of light, an emission source, and to a measurement instrument, hence the application of inappropriate values can introduce significant uncertainties. These uncertainties can be reduced through parallel measurement of light absorption and mass, and through the development and application of robust estimates of mass absorption efficiency.

14 For each measurement technique, proper dilution, cooling and aging of the sample are necessary before measurements are taken. This ensures that the physical and optical properties of an emissions sample reflect changes in morphology, size distribution, mixing state and other properties that occur with exposure to ambient air. A consistent protocol for dilution, cooling and ageing is necessary when comparing measurement techniques.

15 The following describes filter-based and in situ[4] methods for sampling emissions of BC. Widely used techniques in each group are introduced, followed by their application, advantages and disadvantages. Remote sensing is not suitable for direct measurement of ship emissions and is not included here.

Filter-based methods

16 <u>Filter-based methods</u> involve collecting particles on quartz or Teflon filter media, where they are weighed to obtain mass density, or where light absorption is derived from the attenuation of light transmitted or reflected from the loaded filter. Filter sampling is relatively simple, low cost, and widely used. However, measurements are affected by interaction with the filter that causes changes in particle size and morphology. Corrections can be made using assumptions about the effects of filter media and the nature of the particle sample.

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4 Refers to particles suspended in air. See Moosmüller, H., Chakrabarty, R., & Arnott, W. (2009). Aerosol light absorption and its measurement: A review. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *110*(11), 844-878.

17 Transmittance/reflectance methods: particle samples are collected on a single filter or continuously on paper tape. As the particle sample increases, attenuation of a calibrated light source is measured and related to transmittance or reflectance from a blank filter. The Aethalometer and the Particle Soot Absorption Photometer (PSAP) are two instruments that continuously measure transmittance through a filter. The Multi-Angle Absorption Photometer (MAAPS) measures reflectance as opposed to transmittance. These instruments provide high time resolution and can operate for long periods without intervention. The PSAP uses a single filter that needs to be changed, but its small footprint makes it convenient for source sampling. The multi-wavelength Aethalometer AE31, PSAP, and MAAP 5012 are examples of commercial instruments.

18 Thermal speciation methods: particle samples are heated in a stepwise fashion along a pre-defined temperature protocol to incrementally volatilize and oxidize particles with detection of the evolved carbon mass. In this way, the mass of elemental carbon (EC) is captured. The most commonly used thermal methods heat samples in an inert atmosphere such that some of the organic material chars to EC. This charring is monitored by reflected and/or transmitted light to derive a charring correction factor. The protocol used in the United States urban and rural PM2.5 speciation network is the Interagency Monitoring of Protected Visual Environments (IMPROVE_A) protocol. Since initial and final transmittance/reflectance are monitored by IMPROVE_A, a filter attenuation measurement of light absorption would enable an estimate of the mass absorption efficiency for BC from international shipping.

In situ methods

19 An in situ method measures particles suspended in air. This removes uncertainties inherent in artifact corrections needed for filter-based methods. Light absorption can be measured via indications of temperature change after exposure to light. This includes temperature change via the pressure disturbance of surrounding air, the change in the refractive index, or thermal radiation in the visible or near-visible spectrum. Absorption can also be measured by the difference method (i.e. the extinction minus scattering coefficient). The application of these in situ techniques is less widespread due to their higher cost and complexity.

20 Photo-acoustic: photo-acoustic techniques measure audible signals generated by changes in air pressure around a light-absorbing particle. The intensity of the sound wave is proportional to the light absorption of the particle. Technological progress has made this instrument capable of field measurement and detection over a wide range of concentrations and samples; however, the cost and complexity of these instruments have limited their widespread application. In addition, the presence of a significant semi-volatile fraction in a particle sample can reduce accuracy, since evaporation of these particles requires a heat of vaporization that reduces measured absorption. The Micro Soot Sensor (AVL 483) and the Photo-Acoustic Soot Spectrometer (PASS-1 and PASS-3) are examples of photo-acoustic instruments.

21 Refractive index-based: refractive index-based techniques use an interferometer to measure changes in the refractive index of a particle as it changes temperature in response to light absorption. These techniques can measure particle size and light absorption in real time; however, measurement of semi-volatile particles can be a challenge. No commercial instruments are yet available since these instruments remain sensitive to vibration and other environmental factors that cause interference.

22 Laser-induced incandescence: laser-induced incandescence (LII) uses a high-power laser to heat a particle sample to more than 2000 degrees K. The vaporization of the sample produces a signal of incandescence that is measured to estimate particle mass. These instruments can produce real-time measurements and estimates of particle size, as well as particle mass and mixing state. Changes in particle morphology and composition during measurement introduce challenges to measurement interpretation. Experience with LII is currently limited to research applications. The Single Particle Soot Photometer (SP2) is an example of an LII instrument.

23 Difference methods (extinction-minus-scattering): a nephelometer directly measures a scattering coefficient and extinction coefficient of a sample exposed to a light source, and absorption is given as the difference between extinction and scattering. A sufficiently large sample is needed to ensure accuracy, and highly sensitive instruments are needed to measure particles with high single-scattering albedo. For strongly absorbing particles, the nephelometer can suffer from biases. The absorption value can be uncertain since it is estimated from the difference between two large values. No commercial instruments are currently available.

Evaluation of measurement techniques

24 We propose five criteria for comparing techniques:

.1 Sampling: in situ sampling techniques for light absorption measure particles in their natural state and suffer from fewer measurement artifacts. These are preferred over filter-based techniques requiring corrections that may create uncertainty.

.2 Multi-wavelength: multi-wavelength measurements are better able to quantify the full extent of climate impacts of emissions. Methods that can quantify light absorption from 880 to 320 nm would allow BC to be separated from weakly absorbing carbon.

.3 Direct vs. indirect: techniques that make direct measurements are preferred over indirect techniques that must make inferences. Conversion coefficients necessary for indirect techniques may produce additional uncertainty.

.4 Incremental cost and practicality: the method should add a small share to the cost of a source test and should not require special expertise to operate.

.5 Commercial: several instruments are in commercial use, while others are still limited to laboratory applications. Instruments that are commercialized are preferred.

Table 1 – Evaluation of techniques for measurement of BC emissions

	Sampling	*Multi-wavelength*	*Direct*	*Cost*	*Commercial*	*Total*
Transmittance/reflectance	-	+	-	+	+	+++
Thermal speciation	-	-	+	+	+	+++
Photo-acoustic	+	+	+	-	+	++++
Refractive index	+	-	-	-	-	+
Laser incandescence	+	-	+	-	+	+++
Difference	+	-	+	-	-	++

25 All techniques reviewed here generate reasonably precise measurements, provided that proper correction methods are applied. A consistent protocol for dilution, cooling and ageing of particle samples is necessary to enable consistency in measurements.

Recommendations

26 Based on this evaluation, we make the following recommendations:

.1 The photo-acoustic technique is the preferred method for quantifying light absorption of BC. Measurement at multiple wavelengths would provide useful additional data.

.2 Measurement of elemental carbon mass should be conducted in parallel with light absorption of BC. The preferred method for mass measurement is the filter-based thermal speciation method using the IMPROVE_A protocol[5]. Since initial and final transmittance/reflectance is monitored by IMPROVE_A, a filter attenuation measurement of light absorption should be taken to enable an estimate of mass absorption efficiency and to compare this with photo-acoustic measurements.

.3 A review of mass absorption efficiency of BC emissions from international shipping should be undertaken. This review should: make estimates at multiple wavelengths; review results from multiple instruments; and correlate measurements between instruments. Based on this review, a recommendation should be made for international shipping.

.4 A protocol for sampling of emissions from international shipping should be developed. The protocol should include steps for dilution, cooling and aging the sample in order to enable consistent comparison and reporting of measurement results across sampling events. It would also review relevant protocols for measurement of other emission species and ensure compatibility with them.

.5 Appropriate instruments and measurement techniques should be re-evaluated periodically to take into account scientific advances, improvements in engineering and recent commercialization. Some techniques that are currently only available in the laboratory may improve significantly in the coming years.

Action requested of the Sub-Committee

27 The Sub-Committee is invited to note this document and take action as appropriate.

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[5] The existence of the widely applied IMPROVE_A protocol gives this technique added value above others.