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Intercomparison between a single particle soot photometer and evolved gas analysis in an industrial area in Japan: Implications for the consistency of soot aerosol mass concentration measurements

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HIGHLIGHTS

- An SP2 was compared with a semi-continuous EC/OC analyzer.
- The uncertainties with regard to SP2 calibration were revisited.
- Carbon black is another candidate as an SP2 calibration standard.
- rBC mass was consistent with EC mass within the uncertainties related to EGA.
- Differences in thermal-protocols are very important to compare rBC with EC.

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ABSTRACT

Mass concentrations of soot (typically comprising black and elemental carbon; BC and EC, respectively) aerosols, were measured at Yokosuka city, an industrial region in Japan in the early summer of 2014. The results of laser–induced incandescence (LII) and evolved gas analysis (EGA) techniques were compared using a single particle soot photometer (SP2) and semi-continuous elemental/organic carbon analyzer (EC/OC analyzer), respectively. We revisited the procedure of SP2 calibration with a focus on investigating the relationship between LII intensity (S_{LII}) and refractory BC (rBC) mass per particle (m_{PP}) for some BC-proxies in the laboratory, as well as for ambient rBC particles in order to discuss the uncertainty of the SP2. It was found that the m_{PP}–S_{LII} for the fullerene soot and carbon black particles agreed well within 3% and 10%, respectively, with that for ambient rBC particles. This is the first time to suggest the use of carbon black as a reference material. We also found that the m_{PP}–S_{LII} for the aqueous deflocculated Acheson graphite particles with the correction factor given by Baumgardner et al. (2012) was still biased by around +20% to that for ambient rBC particles. EC quantified by the semi-continuous EC/OC analyzer using a thermal-protocol similar to that of Interagency Monitoring of Protected Visual Environments (IMPROVE–like), systematically showed higher concentrations than rBC measured by the SP2. The uncertainties related to SP2 cannot fully account for this difference. This result was likely caused by the contribution of charred organic materials to EC, which can be affected significantly by thermal-protocols for the EGA. The consistency and differences between rBC and EC are discussed with regard to comparing their respective mass concentrations.

1. Introduction

Soot aerosol is one of the most important aerosol classes, affecting the Earth's radiative budget both directly through light absorption and indirectly by acting as cloud condensation and ice

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nuclei (e.g., Bond et al. (2013)). Soot aerosols are often simply referred to as black carbon (BC) or elemental carbon (EC), depending on the analytical method used. Andreae and Gelencśer (2006) suggested that the complexity of carbonaceous aerosols can make it very difficult to clearly separate carbonaceous aerosols into BC/EC and organic carbon (OC), because they include intermediate carbonaceous materials between BC/EC and OC, such as refractory and light-absorbing OC. Petzold et al. (2013) recently reviewed the terminology and definition of BC and EC.

EC represents the carbon content of thermally inert atmospheric aerosol such as graphitic carbon, whereas BC mass concentrations are derived from an optical technique based on the light absorption of particles (e.g., Bond et al., 1999). EC mass concentrations were determined by an evolved gas analysis (EGA) technique combined with optical correction for the EC/OC separation (Birch and Cary, 1996). Light-absorption techniques have been used for the quantification of BC mass concentration (referred to as equivalent black carbon, EBC), which is based on the assumption of a mass absorption cross section, in a wide variety of atmospheric environments because these instruments are generally easy to operate, repeatable, and inexpensive to run on a long-term basis. Note that the mass absorption cross sections were estimated by comparing absorption coefficient and EC mass concentrations. Further to light-absorption techniques, the laser-induced incandescence (LII) method can be used to detect and quantify the mass of refractory BC (rBC) in soot-containing particles (Stephens et al., 2003). The single particle soot photometer (SP2) is a commercially available soot particle analyzer based on the LII method (Droplet Measurement Technologies Inc.; Schwarz et al., 2006; Moteki and Kondo, 2007). Currently, SP2 is recognized as one of the most sensitive and reliable instruments for the characterization of soot-containing particles, because of the rBC mass quantification not strongly dependent of the mixing state of rBC (Moteki and Kondo, 2007) and no large instrumental errors for the SP2 (Laborde et al., 2012). However, a limited numbers of studies have compared the SP2 with other analytical techniques, particularly EGA (Kondo et al., 2011; Laborde et al., 2012, 2013). Furthermore, the effects of differences in the thermal-protocols to the EGA-SP2 intercomparison have never been investigated. The data compatibility of rBC and EC mass concentrations is the most important in providing the consistent and reliable data-sets of rBC/EBC/EC concentrations for model validation, linking emission factors to observations, and analysis of long-term data.

In this study, we report the results from an intercomparison experiment of measurements of soot-containing particles conducted at Yokosuka within the Tokyo–Yokohama industrial region; one of the largest industrial areas in Japan. Multiple analytical methods including an SP2 and semi-continuous EC/OC analyzer were included in the experiments for the intercomparison. We discuss differences between rBC and EC with uncertainties related to both SP2 and EGA. Some of the abbreviations for key parameters used in this study are summarized in Table 1.

Table 1
Summary of abbreviations for key parameters used in this study.

Elemental carbon (EC) analyzer	
M_{TEC}	Mass concentration of Thermal EC
M_{OEC}	Mass concentration of Optical EC
Single Particle Soot Photometer (SP2)	
S_{LII}	Signal intensity of incandescence from rBC-containing particle
N_{rBC}	Number concentration of rBC
M_{rBC}	Mass concentration of rBC
MED	Mass equivalent diameter
Calibration of SP2	
D_{mob}	Electrical mobility equivalent diameter
m_{PP}	Mass per particle

2. Experimental

2.1. Single particle soot photometer

We used an SP2 (SP2-D, Droplet Measurement Technology, Inc., USA), for analyzing the size, mass, and mixing state of single rBC-containing particles. The principle of the SP2 has been described in previous studies (e.g., Schwarz et al., 2006; Moteki and Kondo, 2007). Briefly, the SP2 detects both the light scattering and thermal emission from individual rBC-containing particles illuminated by a near-infrared laser beam (CW, 1064 nm). The mass of rBC for a single particle is derived from the thermal emission (LII signal) intensity of the particles on their incandescence in the laser beam, and is typically calibrated in the laboratory using BC-proxies (Moteki and Kondo, 2010; Gysel et al., 2011). The SP2-community calibrate the LII signal intensities from rBC against particle-mass classified by the aerosol particle mass analyzer (Ehara et al., 1996; APM model 3601; Kanomax Japan, Inc., Japan) or centrifugal particle mass analyzer (Olfert and Collings, 2005; CPMA; Cambustion, Ltd., UK). A calibration procedure in quantifying rBC mass per-particle for the SP2 is revisited in this study to clarify the uncertainty of the SP2, because only two studies, Moteki and Kondo (2010) and Laborde et al. (2012), verified the calibration based on the use of laboratory-generated fullerene soot (FS) particles. We applied a method individually calibrating both the relationships between electrical mobility diameter (D_{mob}) and rBC mass per particle (m_{PP}) and between D_{mob} and LII signal intensities from rBC-containing particles (S_{LII}) in the laboratory. We conducted laboratory experiments characterizing FS (stock 40971, lot L20W054, Alfa Aesar, USA) particles with a differential mobility analyzer (DMA, model 3081, TSI, Inc., USA) and APM (DMA–APM) system (Moteki and Kondo, 2010), and various laboratory-generated and ambient rBC particles by using the DMA and CPMA (DMA–CPMA). The experimental setup for each of the measurements of the D_{mob}–m_{PP} relationship is shown in the supplemental information (SI). A custom-made thermodenuder was used upstream of the DMA to prepare ambient nonvolatile particles for the calibration. Details of the thermodenuder system used in this study are given in subsequent sections. The laboratory-generated rBC particles included FS, aqueous deflocculated Acheson graphite (Aquadag; lot 9627, Acheson Inc., USA), and carbon black (CB; stock 45527, lot D30Z059, Alfa Aesar, USA). The combination of two relationships, m_{PP}–D_{mob} and S_{LII}–D_{mob}, enabled us to calculate the size-resolved rBC number and mass concentrations (N_{rBC} and M_{rBC}, respectively) based on a calibration without the use of APM or CPMA. Such S_{LII}–D_{mob} calibrations were regularly performed prior to laboratory or atmospheric deployments of the SP2, whereas the m_{PP}-D_{mob} calibration was performed in the laboratory because of the limited availability of APM or CPMA compared to DMA. The sensitivity of these soot-proxies to the quantification of m_{PP} are revisited in this study. The S_{LII}–m_{PP} relationships for the tested soot particles were compared with those for ambient soot particles at the site close to the source region.

We calculated the time-resolved rBC number– and mass–size distributions for the particle size range 80–400 nm (mass equivalent diameter, MED). The mass fractions not measured by SP2 were estimated by fitting a lognormal distribution to the observed size distribution and extrapolating this fit to the outsides of lower and larger boundaries. (The mean correction factor is 1.18 (±5%).) The mixing states of rBC were also analyzed based on the evolution of the light scattering and thermal emission signals from rBC-containing particles. The time difference between the peaks in the light scattering and thermal emission signals (commonly