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Physicochemical and optical properties of combustion-generated particles from a coal-fired power plant, automobiles, ship engines, and charcoal kilns

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ABSTRACT

The physicochemical and optical properties of combustion-generated particles from various sources were investigated. Coal-fired power plants, charcoal kilns, automobiles, and ship engines were the major sources, representing combustions of coal, biomass, and two different types of diesel, respectively. Scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and energy-dispersive X-ray spectroscopy (EDX) equipped with both SEM and HRTEM were used for physicochemical analysis. Light-absorbing properties were assessed using a spectrometer equipped with an integrating sphere.

Particles generated from different combustion sources and conditions demonstrate great variability in their morphology, structure, and composition. From coal-fired power plants, both fly ash and flue gas were mostly composed of heterogeneously mixed mineral ash spheres, suggesting that complete combustion released carbonaceous species at high temperatures (1200–1300 °C). Both automobile and ship exhaust from diesel combustion show the typical features of soot: concentric circles comprising closely packed graphene layers. However, heavy fuel oil (HFO)-combusted particles from ship exhaust demonstrate more complex compositions containing a different morphology of particles than soot; for example, spherically shaped char particles composed of minerals and carbon. Regarding soot aggregates, particles from HFO combustion have different chemical compositions; carbon dominates but Ca (29.8%), S (28.7%), Na (1%), and Mg (1%) are also present, which were not found in particles from automobile emission. This indicates that fuel properties and combustion conditions are important in determining the fate of particles. Finally, from biomass combustion, amorphous and droplet-like carbonaceous particles with no crystalline structure were observed, and are generally formed by the condensation of low-volatile species at low-temperature (~300–800 °C) combustion conditions. Significant differences in optical properties depending on the combustion source were observed. Diesel combustion particles from automobile and ship showed wavelength-independent absorbing properties, whereas the particles from coal and charcoal kiln combustion showed enhanced absorption at shorter wavelengths, which is a characteristic of brown carbon. Main light absorbers at short wavelengths are proposed for organics and minerals (e.g., iron oxide) for biomass and coal combustion, respectively. Our findings suggest that source-dependent properties and distributions across the globe should be considered when their impacts on climate change and air qualities are discussed.

1. Introduction

Combustion-generated particles are important constituents of ambient particulate matter [1–5], and substantial contributors to climate forcing that leads to the cooling or warming of the Earth's surface by the net effect of scattering or absorbing properties of aerosols [5]. Black carbon (BC) or soot is one of the most important combustion-generated particles, and originates primarily from diesel, gasoline, biomass, and organic wastes, and representative species in the atmosphere that absorb light over the entire visible spectrum [4,6]. Brown carbon (BrC) is also important but mostly emitted by inefficient combustion of hydrocarbons (e.g., smoldering) from biomass combustion [7]. BrC is a part of organic aerosol that is known for scattering carbonaceous particles in the atmosphere; however, unlike those organic aerosols, BrC has strong

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absorbing properties near the UV range of the spectrum, resulting in its brown color [8,9]. However, determination of the atmospheric roles and climate effects of those carbonaceous particles is difficult because their mixing status and properties in the atmosphere vary according to their source and combustion conditions [2,10]. It is, therefore, essential to identify the physical, chemical, and optical properties of carbonaceous species associated with their sources and combustion conditions in evaluating their effects and improving climate predictions. Investigating these properties further provides useful information on reactivity, formation processes, and eventually the fate of these species in the atmosphere [11]. Current knowledge on such issues has limitations in terms of developing an accurate representation of carbonaceous species in models and anticipating their impacts on the atmosphere.

One of the advanced techniques for measurement of the bulk and surface properties of particle is electron microscopy, such as high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) [12]. A few studies have used these methods to characterize the properties of particles, investigating the size, morphology, chemical composition, and mixing state of carbonaceous species to distinguish several different types [13–16]. Energy-dispersive X-ray (EDX) microanalysis equipped with HRTEM and SEM further allows identification of the spatially resolved chemical compositions of individual particles [17,18]. Furthermore, TEM imaging with electron energy-loss spectroscopy (EELS) can be used to characterize the carbon content of particles [17]. Microscopy has revealed that properties vary depending on aerosol sources, formation temperatures, combustion conditions or condensation, and evaporation of primary and secondary gases [19–22]. However, most previous studies have focused on the characterization of particles from one specific source; therefore, comparisons of different combustion sources are lacking [16,23–25]. Some studies have used laboratory-generated carbonaceous particles (e.g., lamp black or lab-generated wood smoke) in the chamber to mimic BC or BrC [26–28], leaving some gaps regarding the properties of real carbonaceous particles in the atmosphere.

To investigate how different sources and formation processes of carbonaceous species determine their characteristics in the real atmosphere, in this study, we collected particles directly from specific sources such as coal-fired power plants, automobiles, ship engines, and charcoal kilns as representative sources involving the combustion of coal, different types of diesel, and biomass, respectively. These are substantial sources of carbonaceous species globally and exhibit some spatial variations [29]. For example, the power plant is one of the largest contributors to air pollutants, and East Asian power generation is dominated by coal-fired power plants, whereas biomass combustion is the main source of BC in Africa and Latin America [30]. Furthermore, Europe, North America, and Latin America have a high fraction of BC from diesel combustion, which is an important emission source, especially in urban areas [29]. In addition, BC from ship exhaust is increasingly understood as a main cause of warming in the Arctic [31].

Besides physicochemical characterizations using HRTEM, SEM, and EDX, the fundamental mechanisms of particle formation associated with combustion conditions and sources and, further, their impacts on optical properties, were investigated.

2. Experimental

2.1. Sampling sources

Combustion conditions of four different sources vary depending on the fuel used (Table 1), temperature range 800–2000 °C under normal to high pressures. Note that seasonal and diurnal running conditions of each source are almost constant throughout the year, as well as particles are sampled directly from sources, and therefore the properties of the particles were not influenced by the sampling period. Detailed descriptions of running conditions are as follows.

Table 1
Fuel types and combustion conditions of the emission sources investigated.

Emission sources	Fuel	Combustion condition		Sampling in this study
		Temperature	Pressure	
Coal-fired power plant	Coal (Subbituminous coal)	1200–1300 °C	Normal pressure	Fly ash Stack flue gas
Charcoal kiln	Wood (oak)	Maximum 800 °C	Normal pressure	Stack flue gas
Diesel vehicle	Diesel	~2000 °C	High pressure	Tunnel sampling
Ship engine	HFO (Heavy Fuel Oil)	~2000 °C	High pressure	Flue gas

Particles from coal combustion were sampled at the Samcheonpo coal-fired power plant located in Goseong, South Korea. Samcheonpo power plant, which is composed of four 560-MW plants and two 500-MW plants, is one of the largest power plants in Korea. Sampling was conducted from flue gas from the stack and fly ash after combustion. Combustion temperatures varied between 1200–1300 °C and 1400–1500 °C depending on the composition of the coals. In this study, subbituminous coal was sampled from the fifth plant running at 1200–1300 °C. Particles from diesel combustion were investigated from automobile and ship emissions using diesel and heavy fuel oil (HFO), respectively. Particles from automobiles were sampled from Moran Tunnel (two lanes 1598 m long, 7 m high, and 8.6 m wide) located at Namyangjoo–Si in Korea to collect diesel-generated particles emitted under real driving conditions, rather than an automobile-testing setup such as a dynamometer, which is usually used to obtain diesel-surrogate particles. Particles sampled at the Moran Tunnel could be assumed to be generated by diesel automobiles, because automobiles running through Moran Tunnel are mostly heavy-duty diesel trucks. For particles burned from HFO, samplings were performed onboard the selected ship, the 6686-ton Hanbada, which is 117.2 m long, 17.8 m wide, and 8.15 m deep, with an 8130-BHP (79.75-MW) engine. To investigate the properties of particles sampled under real conditions, samplings took place under driving conditions at 176 rpm. The particles were collected on a metal pipe probe stacked into the exhaust pipeline approximately 25 m behind the engine. For particles from biomass combustion, a charcoal kiln was used as a representative source for Korea. Unlike in other countries where residential heating is the main purpose of burning wood, the need for charcoal derived from wood burning is high in Korea, mainly for cooking of meat. Because of the high demand, kilns run throughout the year so that wood burning-generated particles are significant throughout the year. Table S1 shows the number of kilns still running in Korea. A kiln located in Gyeonggi province, which has the highest charcoal production, was selected. Charcoal is still produced by traditional methods using kilns to conserve the quality of the charcoal. Two main stages are required to produce charcoal: the initial stage and the maintenance stage. At the initial stage, wood burning is initiated and the kiln is covered with small holes allowing only a minimal amount of oxygen to be provided for two to three days. During the following maintenance stage, the kiln is kept burning for three days, and the small holes are covered to prevent access to oxygen. The highest temperature reached in the kiln is around 800 °C, and the average combustion temperature at the initial stage is around 350 °C. Particles emitted by wood burning were collected at the initial stage when most efficient burning occurred with oxygen providing in order to collect representative particles of biomass combustion.