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Physicochemical characterization of aged biomass burning aerosol after long-range transport to Greece from large scale wildfires in Russia and surrounding regions, Summer 2010

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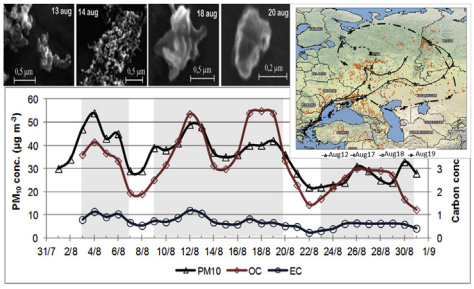
HIGHLIGHTS

- Transport of biomass burning aerosol from Russia/Ukraine to Athens was documented.
- Oxidized soot particles of high organic carbon content were observed in aged smoke.
- Formation of secondary organics and ammonium sulfate/nitrate during smoke aging.
- Shift of size distributions towards larger particles for aged smoke aerosol.
- Results suggest entrainment and long-range transport of soil dust during wildfires.

GRAPHICAL ABSTRACT



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ABSTRACT

Smoke aerosol emitted by large scale wildfires in the European part of Russia and Ukraine, was transported to Athens, Greece during August 2010 and detected at an urban background site. Measurements were conducted for physico-chemical characterization of the aged aerosol and included on-line monitoring of PM_{10} and carbonaceous particles mass concentrations, as well as number size distributions and aerosol optical properties. In addition TSP filter samples were analyzed for major inorganic ions, while morphology and composition of particles was studied by individual particle analysis. Results supported the long-range transport of smoke plumes from Ukraine and Russia burning areas indicated by back trajectory analysis. An increase of 50% and 40% on average in organic (OC) and elemental carbon (EC) concentrations respectively, and more than 95% in carbonate carbon (CC) levels was observed for the biomass burning (BB) transport period of August with respect to the previous month of July. Mean 24-h OC/EC ratio was found in the range 3.2–8.5. Single scattering albedo (SSA) was also increased, indicating abundance of light scattering constituents and/or shift of size distributions towards larger particles. Increase in particle size was further supported by a decreasing trend in absorption Angström exponent (AAE). Ion analysis showed major contribution of secondary species (ammonium sulfate and nitrate) and soil components (Ca^{2+}, Mg^{2+}). Non-sea salt K^{+} exhibited very good correlation with

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secondary species, indicating the long-range transport of BB smoke as a possible common source. Individual particle analysis of the samples collected during BB-transport event in Athens revealed elevated number of soot externally mixed with fly ash Ca-rich particles. This result is in agreement with the increased OC and CC levels measured, thus pointing towards the main components comprising the aged BB aerosol microstructure.

1. Introduction

Large amounts of air pollutants are released worldwide by biomass burning (BB) processes, including wildfires, prescribed burnings (agricultural waste, etc.) as well as domestic biofuel combustion. Open biomass burning relating to deforestation, grass burning, and vegetation fires contributes as much as 42% to the combustion emission global inventory accounting burning areas and wildfire counts (Bond et al., 2013). BB emissions contain several hundreds of compounds including particulate matter (PM), carbon monoxide (CO), polycyclic aromatic hydrocarbons (PAHs), aldehydes, and semivolatile and volatile organic compounds (VOCs) (WHO, 1999). BB smoke is formed from the condensation of volatilized organic and inorganic compounds; its properties vary significantly depending on burning conditions such as type of fuel, combustion phase, and meteorological conditions (Reid et al., 2005a). Different types of carbonaceous particles may be identified in biomass smoke based on composition and morphology, such as soot and organic particles with inorganic inclusions dominated by potassium, chlorides and sulfates (Posfai et al., 2003; Osan et al., 2002). Soot produced by open fires generally presents an EC content of 5–10% (Reid et al., 2005a). Emission of soil dust may be also observed during wildfire events, due to the increased turbulent mixing near the fire front (Kavouras et al., 2012; Samsonov et al., 2005). This effect may be enhanced during large wildfires accompanied by strong winds, when increased fuel loads and higher burning temperatures result as well in higher shear stresses at the soil surface.

Large-scale BB events are considered one of the main sources of atmospheric pollutants, influencing local and regional air quality, with significant implication to visibility, ecosystems, human health, global radiation budgets, and climate (Andreae and Merlet, 2001). Exposure to smoke plumes produced by massive fire events has been linked with adverse health effects that range from minor irritation of the eyes and respiratory system to increased rates of hospital admissions for respiratory diseases and mortality (Naeher et al., 2007). BB aerosol has been demonstrated to present greater toxicity level than ambient urban aerosol (Wegesser et al., 2009). In addition, BB aerosol may significantly alter the Earth's radiation by scattering and absorbing solar radiation (Lewis et al., 2008). Its effects are both short- and long-term, since increased light scattering by particles cools the Earth's surface but increased CO_2 warms the surface in the long-term. Biomass burning particles can also affect climate indirectly by acting as cloud condensation and ice nuclei and modifying cloud microphysics and reflectivity (Yun et al., 2013; Reid et al., 2005a).

BB plumes may be advected over very long distances by entering the free troposphere, where pollutants' transport is more efficient than in the mixed layer due to fewer loss mechanisms and stronger winds (Holloway et al., 2003). Several studies have demonstrated significant impact of wildfire events on ambient levels within urban centers situated thousands of kilometers away from the fires (Saarikoski et al., 2007; Niemi et al., 2005; Sapkota et al., 2005). In this framework, monitoring of BB aerosol physico-chemical and optical properties and understanding its aging processes are essential in assessing the effect of biomass burning emissions at regional and global scale (Saarnio et al., 2010; Engling et al., 2006). Chemical composition, size, and mixing state of BB aerosol, all properties closely related to their impact on health and the environment, may differ significantly for particles above fire, after processing in urban atmosphere or aged smoke plumes transported over long distances. Several studies have reported increased formation of secondary organic aerosol (SOA) during the aging of BB emissions (Adler et al., 2011; Grieshop et al., 2009). Coagulation and gas-to-particle conversion result in increase of particle size, leading to enhanced scattering and reduced absorption of aged BB aerosol, in relation to freshly emitted smoke (Reid et al., 2005b). It has been also indicated that aged soot is heavily internally mixed and that this may affect the heterogeneous chemistry on particles' surface, altering as well their interaction with water, susceptibility for washout, and hence lifetime (Johnson et al., 2005).

Changes in global climate have lead to an increase of the frequency of heat waves and similarly of extensive fire events across Europe (Della-Marta et al., 2007; Tebaldi et al., 2006). Summer 2010 brought an unusual heat into Eastern Europe; the existing record of 36.8 °C set back in 1920 had been broken several times (Barriopedro et al., 2011; Grumm, 2011). Russia has experienced the worst drought since 1972 collocated with anomalous anticyclonic circulation. Heat and dry conditions provoked numerous wildfires of forest, peat bogs, and infrastructure (Bondur, 2010). Extensive fires occurred in the Moscow region starting in late July 2010, with strong impact on smoke microstructure, aerosol chemistry, and air quality of the megacity's atmosphere (Popovicheva et al., 2014a). Continuously spreading fires resulted in high gaseous and particulate emissions which, transported through the atmosphere, caused episodes of extreme air pollution in many parts of Russia, and other European counties, such as Ukraine, Estonia and Finland (Portin et al., 2012; van Donkelaar et al., 2011; Konovalov et al., 2011; Mei et al., 2011).

This work focuses on the physico-chemical characterization of aged smoke aerosol transported from extensive wildfires in the European part of Russia and Ukraine to Athens, Greece during August 2010. Real time monitoring of aerosol optical properties, PM_{10} and carbonaceous particles concentrations has been combined with chemical speciation techniques, including individual particle microstructure analysis, in order to examine the nature of smoke-affected particles and reveal the morphology and specific chemical features of aerosol in the BB plumes after long-distance transport and transformation.

2. Materials and methods

2.1. Site description

Measurements were conducted at the N.C.S.R. “Demokritos” campus (37° 59′ N, 23° 48′ E, 270 m a.s.l.), in the North East corner of the Greater Athens Area. Aerosol physico-chemical properties are continuously monitored at the Demokritos GAW suburban background station since 2007 (GAW-DEM, 2007). The station lies in a field site away from direct emission sources in a vegetated area.