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Black carbon in soils from different land use areas of Shanghai, China: Level, sources and relationship with polycyclic aromatic hydrocarbons

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ABSTRACT

Black carbon (BC) in soils plays a key role of carrying hydrophobic pollutants like polycyclic aromatic hydrocarbons (PAHs). However, little is known about the spatial distribution, sources of BC and its relationship with PAHs in urban soils. We studied BC, total organic carbon (TOC) and PAHs concurrently in 77 soils collected from downtown area, suburban and rural area and industrial area of Shanghai, China. BC was determined by both chemical oxidation (dichromate oxidation, BC_{Cr}) and chemo-thermal oxidation (CTO-375, BC_{CTO}). BC sources were identified qualitatively by BC/TOC concentration ratios and BC-cogenerated high molecular weight (HMW) PAH isomer ratios and quantitatively by principal component analysis followed by multiple linear regression (PCA-MLR). Results showed that BC_{Cr} concentration (4.65 g/kg on average) was significantly higher than BC_{CTO} (1.91 g/kg on average) in Shanghai soils. BC_{Cr} concentrations in industrial area were significantly higher than those in other two. Stronger correlation was found between PAHs and TOC, BC_{Cr} than that between PAHs and BC_{CTO}, which indicates the possibility of PAHs being carried by charcoal and other organic matters thus negating its exclusive dependence on soot. Charcoal was therefore suggested to be taken into account in studies of BC and its sorption of PAHs. BC/TOC ratios showed a mixed source of biomass burning and fossil fuel combustion. PCA scores of BC-cogenerated HMW PAHs isomer ratios in potential sources and soil samples clearly demonstrated that sources of BC in urban soils may fall into two categories: coal and biomass combustion, and traffic (oil combustion and tire wear). PCA-MLR of HMW PAHs concentrations in soil samples indicated that coal and oil combustion had the largest contribution to BC in urban soils while tire wear and biomass combustion were important in downtown and rural area, respectively, which indicated they were main sources of HMW PAHs and presumably of BC.

1. Introduction

Black carbon (BC) is the carbonaceous residue (e.g., charcoal) or condensate (e.g., soot) generated from incomplete combustion of fossil fuels and biomass. A quantity of 62–294Tg BC were produced per year, of which 80–90% were deposited directly in soils (Druffel, 2004) and the rest were emitted into atmosphere followed by further deposition after transportation. BC in soil may adsorb hydrophobic organic compounds (HOCs) and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs) (Koelmans et al., 2006) and by carrying toxic pollutants, it results in potential human health risk.

BC in agricultural soil, forest soil and grassland soil has been widely investigated and studied in last decades (Skjemstad et al., 2002; Rumpel et al., 2006; Czimczik et al., 2003; Yin et al., 2009; Ansley et al., 2006; Dai et al., 2005). However, little was known about BC in urban soil especially in metropolises. In an ancient city of China, He and Zhang (2009) investigated BC concentrations in soil profiles from an ancient residential area (0.91 g/kg on average) and a present industrial area (8.62 g/kg on average) and found that BC in the surface layer of soils was mainly from diesel emission while in cultural layers BC was from historical coal use. A study of soot BC in soils from Phoenix, Arizona showed that BC concentrations ranged from 0.2 to 5.4 g/kg and were higher in urban soils than in desert or agricultural soils (Hamilton and Hartnett, 2013). Similarly, concentrations of BC from urban roadside topsoil (a median of 21.8 g/kg) were significantly higher than local background value (3.8 g/kg) in Xuzhou, China (Wang, 2010). Given its complexity of sources and potential risk to residents' health, BC in urban soil should receive more attentions.

BC in soil can be determined by several methods (Hammes et al., 2007). Thermal oxidation (e.g. CTO-375) and chemical oxidation (e.g. Cr_2O_7 oxidation) were representative methods to isolate the most resistant fractions of BC continuum (Masiello, 2004). As

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each method detected different parts of BC continuum, the results varied widely. BC concentrations varied by a factor of up to 500 when different analytic methods were applied to the same soil sample (Schmidt et al., 2001). To eliminate such uncertainty and enhance the reliability of interpretation, method comparison was used in a method study (Roth et al., 2012) as well as environmental monitors (Brändli et al., 2009; Sánchez-García et al., 2013).

PAH was regarded as the precursor of soot, a type of BC, generated during incomplete combustion (Vander Wal et al., 2007). The environmental behaviors and bioavailability of PAHs were strongly affected by BC (Gustafsson et al., 1997; Koelmans et al., 2006). However, among the numerous studies of PAHs in urban soils, few took BC into account. Liu et al. (2011) reported a significant correlation between concentrations of BC and PAHs in the urban area in Beijing, China and there was no such significant correlation found in the rural mountainous area. Ray et al. (2012) observed significant correlations between PAHs and BC in Delhi, India and suggested similar sources of PAHs and BC. Furthermore, most researches of BC and PAHs analyzed BC by method CTO-375 (Liu et al., 2011; Mai et al., 2003). It is soot that the method isolates from BC continuum, while charcoal is oxidized during the analytical procedure. Neglect of charcoal may result in incomprehensive understanding about the relationship between BC and PAHs, since studies have proved that biochar, a type of charcoal, may carry considerable amount of PAHs (Hale et al., 2012; Hilber et al., 2012; Keiluweit et al., 2012).

BC in urban soil may come from both natural and anthropogenic burning of biomass and fossil fuels. Source identification of BC in urban soil is challenging but important. Several methods have been employed to identify the source of BC in soils and sediments, including the use of ^{14}C analysis, ^{13}C analysis, BC/OC ratio, PAH isomer ratio, particle size, morphological characteristics and benzene polycarboxylic acid (BPCA) ratio (Wang, 2012). Despite the higher reliability of radiocarbon and isotopic analysis, other methods were more wildly used for their credibility and less cost. BC/OC ratio method was based on the fact that simultaneous emission of BC and other organic compounds from combustion caused certain BC/OC ratio in aerosol (Gatari and Boman, 2003; Novakov et al., 2000). The ratio was later successfully applied for BC source identification in urban soil and forest soil (Liu et al., 2011; Yin et al., 2009). Some PAH especially high molecular weight (HMW) PAH isomer ratios were believed to reflect combustion sources for the isomer signatures remain when the compounds enter environment (Dickhut et al., 2000). The HMW PAH isomer ratios were used as indicators of sources of PAHs and cogenerated BC during combustion (Mitra et al., 2002).

This paper (i) studies the level and distribution of BC analyzed by two different methods; (ii) identifies BC sources by various methods; and (iii) shows the relationship between BC and PAHs in metropolitan soils under different land use categories.

2. Materials and methods

2.1. Study area and soil sampling

Shanghai is the biggest city and one of the most important industrial centers of China. According to Shanghai Statistical Yearbook (Shanghai Bureau of Statistics, 2012), Shanghai had a population of 23.5 million with a population density of 3702 per square kilometer in 2011. In the same year, Shanghai's vehicle parc reached 3.29 million units and its energy end-use consisted of 9.58 million tons of raw coal, 7.06 million tons of coke, 10.06 million tons of gasoline and diesel oil and 12.46 million tons of other petroleum products.

Soil samples were collected in 2012 (Fig. 1). Seventy-seven sampling sites covered three kinds of land use in Shanghai: downtown

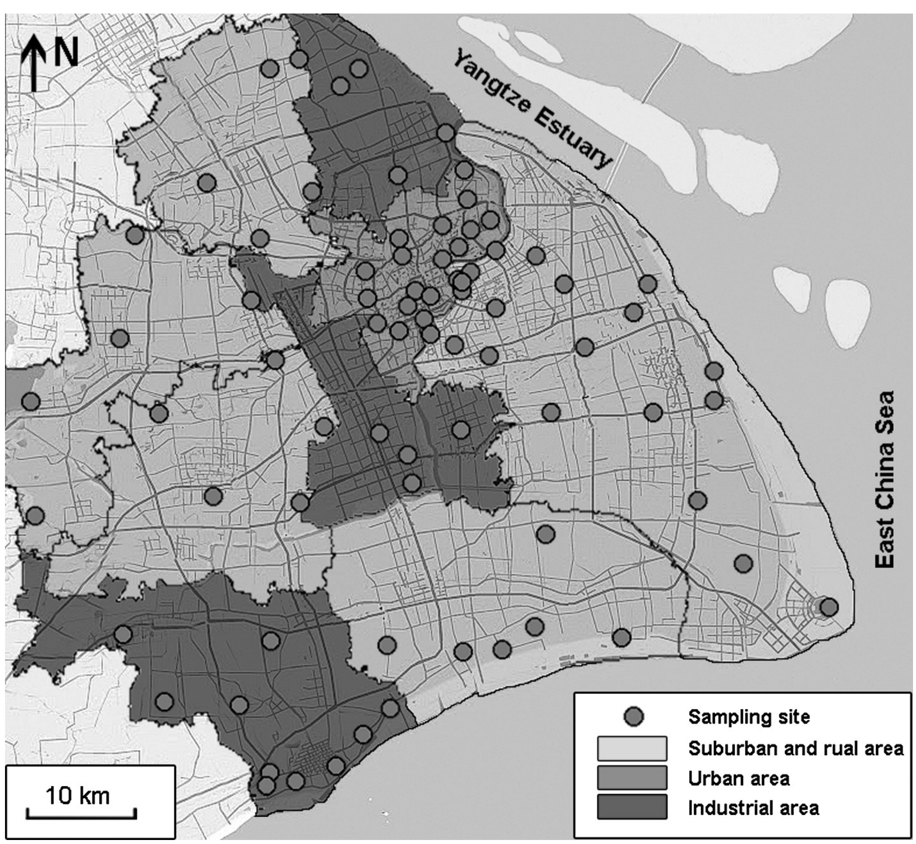

Fig. 1. Schematic map of study area and sampling sites in Shanghai, China.