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Emission of volatile organic compounds from domestic coal stove with the actual alternation of flaming and smoldering combustion processes☆

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ABSTRACT

Volatile organic compounds (VOCs) emissions from the chimney of a prevailing domestic stove fuelled with raw bituminous coal were measured under flaming and smoldering combustion processes in a farmer's house. The results indicated that the concentrations of VOCs quickly increased after the coal loading and achieved their peak values in a few minutes. The peak concentrations of the VOCs under the smoldering combustion process were significantly higher than those under the flaming combustion process. Alkanes accounted for the largest proportion (43.05%) under the smoldering combustion, followed by aromatics (28.86%), alkenes (21.91%), carbonyls (5.81%) and acetylene (0.37%). The emission factors of the total VOCs under the smoldering combustion processes (5402.9 ± 2031.8 mg kg^{-1}) were nearly one order of magnitude greater than those under the flaming combustion processes (559.2 ± 385.9 mg kg^{-1}). Based on the VOCs emission factors obtained in this study and the regional domestic coal consumption, the total VOCs emissions from domestic coal stoves was roughly estimated to be 1.25 × 10^8 kg a^{-1} in the Beijing-Tianjin-Hebei region.

1. Introduction

Coal is the prevailing energy for heating in winter over the vast rural areas in the north of China and its consumption has evidently increased with the increase in residents' income in recent years (Ben and Kayoko, 2015). Ten years ago, small and simple coal stoves were manually made by bricks and fuelled by anthracite coal for heating, and the coal consumption of each family was usually less than 1 ton during the entire winter. In recent years, larger commercial coal stoves fuelled by bituminous coal have been increasingly adopted by residents, with a coal consumption of 2–4 tons per family during the wintertime. Because the combustion efficiency of current domestic coal stoves is very low and no control measures have been adopted (Bond et al., 2004; Finkelman et al., 1999, 2002), smoke from the chimneys of the stoves can be seen everywhere in the rural areas of Beijing-Tianjin-Hebei during the winter season. Various pollutants have been identified in the fluegas from domestic stoves, including particulate matter (PM), polycyclic aromatic hydrocarbons (PAHs), carbon monoxide (CO), sulfur dioxide (SO_2) and so on, which are harmful to human health (Chen et al., 2004, 2005; Huang et al., 2014a; Lee et al., 2005; Oros and Simoneit, 2000; Pandit et al., 2001; Tian et al., 2008; Vanker et al., 2015; Wang et al., 2016; Zhang et al., 2012; Zhang and Smith, 2007). It has been found that indoor air pollution levels (e.g., PM and SO_2) in households using coal for heating or cooking generally exceed that of China's indoor air quality standards, and several investigations have indicated that household smoke is associated with health effects such as respiratory illnesses, lung cancer, chronic obstructive pulmonary disease, weakening of the immune system, etc. (Barreca et al., 2014; Dong et al., 2013; Hosgood et al., 2011, 2013; Subbaraman, 2014; Zhang and Smith, 2007). The pollutants emitted from domestic coal stoves not only threaten the health of residents, but also deteriorate the regional air

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quality (Gaffney and Marley, 2009). Previous studies revealed that the emission factors (EFs) of particulate matter with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$), PAHs, COS and CO from domestic coal stoves were approximately 1-3 orders of magnitude greater than those from power plants (Zhang et al., 2000, 2008; Du et al., 2016). Considering the domestic coal consumption accounts for 11% (4.2×10^{10} kg a^{-1}) of the total coal consumption in the area of Beijing-Tianjin-Hebei (http://www.qstheory.cn/st/dfst/201306/t20130607_238302.htm), the impact of the emissions of various pollutants from domestic coal stoves on the regional air quality have aroused great concern (Boynard et al., 2014; Li et al., 2015, 2014a, 2014b; Liu et al., 2008a; Tao et al., 2012; Xu et al., 2011).

Besides $PM_{2.5}$, PAHs and CO, remarkable emissions of volatile organic compounds (VOCs, non-methane hydrocarbons (NMHCs) and carbonyls) from domestic coal stoves have also been reported (Zhang et al., 2000; Tsai et al., 2003; Wang et al., 2013). After releasing into the atmosphere, VOCs can be oxidized by OH, NO_3 and O_3 to form various secondary pollutants (such as peroxides, secondary organic aerosol (SOA), carbonyls, O_3) that deteriorate the air quality, as well as harm human health and vegetation (Huang et al., 2014b). In addition, some VOCs (e.g., benzene and formaldehyde) emitted from domestic coal combustion have been verified to be toxic, carcinogenic or mutagenic (Møller et al., 2008). However, few studies have investigated VOCs emissions from domestic coal stoves, and those that did only focused on the flaming combustion process (Zhang et al., 2000; Tsai et al., 2003; Wang et al., 2013). Actually, coal combustion in domestic coal stoves usually occurs through alternation of the flaming and smoldering combustion processes in rural areas. Compared with the flaming combustion process, which uses sufficient air supply, the evident decrease in air supply during the smoldering combustion process can result in the flameless burning of coal, slow rate of coal combustion and low temperature of hearth. As many factors, including temperature, air supply, and flame affect VOCs emissions from coal combustion (Oros and Simoneit, 2000; Gaffney and Marley, 2009), VOCs emissions from domestic coal stoves, based on a kind of flaming combustion process, were not suspected to be representative of actual emissions.

To reflect actual VOCs emissions from domestic coal stoves, we investigated the emission characteristics, composition and emission factors (EFs) of VOCs from a prevailing domestic stove fuelled with raw bituminous coal under flaming and smoldering combustion processes in a farmer's house. In addition, the regional VOCs emission from domestic coal combustion was roughly estimated based on the VOCs emission factor and the domestic coal consumption.

2. Experimental section

2.1. Stove and coal

A kind of prevailing stove (Fig. 1a) used by residents for heating during winter in the rural areas of Beijing-Tianjin-Hebei was selected for this study. The stove consists of a hearth, fire grate, an ash door, a heat exchanger and a chimney. The hearth (approximately 18.5 L for loading coal) is located at the centre of the stove and is surrounded by a thermal-insulated ceramic liner which is covered by a metallic outer cover. The fire grate is at the bottom of the hearth for supporting lump coal and felling the ash of the coal combustion. The ash door is under the fire grate for removing the ash and controlling the air flow for combustion. The heat exchanger is on the top side of the metallic outer cover to supply heat for an area of approximately 150 m^2. The chimney (12 cm in I.D. and 6 m in length) is connected with the heat exchanger to drive the air from the ash door through the hearth for coal combustion. Besides heating, the stove is also used for cooking by residents in the morning, noon and evening when the ash door of the stove is fully opened for fast combustion (designated as the flaming combustion process). The fire in the stove was usually kept from extinguishing after ignition by residents during the entire winter, and hence the ash door is always closed (called the smoldering combustion process) after cooking to save coal and labour. Bituminous coal from Inner-Mongolia is currently the prevailing coal used for heating by the residents in the rural areas of Beijing-Tianjin-Hebei. Large blocks of bituminous coal were broken into pieces of 1–5 cm in diameter, and lumps of diameters greater than 3 cm (Fig. 1b) were used for the flaming combustion process; Smaller lumps (Fig. 1c) were loaded into the stove for the smoldering combustion process.

2.2. Sampling

VOCs emissions from the chimney of the stove were investigated in the house of a Dongbaituo village resident in Hebei Province during the winter of 2013, and coal combustion in the stove strictly followed the operation habit of local residents, alternating the flaming combustion process and smoldering combustion process. A stainless-steel tube was inserted into the centre of the chimney, 20 cm below the top of the chimney to collect the air samples, and each air sample was collected into a vacuum SUMMA canister (3.2 L, Entech Inc.) after passing through a filter (0.45 μm). To reflect the VOCs emissions from coal combustion in the stove, a series of air samples from the chimney were collected at different intervals, with a high sampling frequency at the beginning of each coal loading when the smoke was strongest. The carbonyls in the flue-gas were collected with 2,4-dinitrophenylhenylhydrazine (DNPH)-coated Sep-Pak silica gel cartridges. Every 1000 cm^3 gas was sampled into the coated cartridge. After sampling, the cartridges were immediately sealed with silicon caps, and stored in a refrigerator before analysis. A thermocouple was inserted into the chimney (20 cm below the top of chimney) to measure the temperature of the flue-gas. A hand-held velocity meter (Testo 410, Germany) was used to measure the flow rate of the flue-gas.

2.3. VOCs measurements

The air samples were analyzed by a gas chromatography equipped with a flame ionization detector (GC-FID) after preconcentration/thermal-desorption. Details about sample analysis and calibration can be found in Liu et al. (2016). Briefly, 5 or 10 cm^3 of the air samples were injected into a 100 cm^3 syringe which contained high purity N_2, and enriched into an adsorption tube filled with 60–80 mesh Carbopack™ B at 183 K. Then, the adsorption tube was quickly heated to 423 K and the desorbed NMHCs were injected into a capillary column (OV-1, 30 m × 0.32 mm I.D.) for separation: 3 min at 213 K, ramp at 12 K min^{-1} to 253 K, ramp at 6 K min^{-1} to 303 K, ramp at 10 K min^{-1} to 443 K, then hold for 2 min. The NMHCs were detected by FID at 523 K. The standard calibration curves derived from the enrichment of the standard gas mixture of 57 NMHCs (~1.0 ppmv for each NMHC, provided by Spectra Gases Inc., USA) were found to be in good linear correlations ($R^2 > 0.99$); These curves were used for the quantification of the air samples. The method detection limit (MDL) for each species ranged from 2 to 10 ppbv, and the relative standard deviation (RSD) was less than 5%.

The analysis procedure of atmospheric carbonyls was based on the EPA TO-11A method (EPA, 1999), and the details have been described in our previous publications (Pang and Mu, 2006, 2007). The carbonyl derivatives in each DNPH cartridge were eluted slowly with 5.0 cm^3 acetonitrile, and analyzed by an HPLC system (Waters Alliance 2695, USA) with a Supelcosil LC-18 reverse phase column

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