Organic and inorganic speciation of particulate matter formed during different combustion phases in an improved cookstove

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ABSTRACT

Residential solid fuel combustion in cookstoves has established health impacts including bladder and lung cancers, cataracts, low birth weight, and pneumonia. The chemical composition of particulate matter (PM) from 4 commonly-used solid fuels (coal, dung, ambient/dry applewood, and oakwood pellets), emitted from a gasifier cookstove, as well as propane, were examined. Temporal changes between the different cookstove burn-phases were also explored. Normalized concentrations of non-refractory PM_1, total organics, chloride, ammonium, nitrate, sulfate, and 41 particle-phase polycyclic aromatic hydrocarbons (PAHs) were measured using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Thermal desorption Aerosol Gas chromatograph (TAG), respectively.

Coal demonstrated the highest fraction of organic matter in its particulate emission composition (98%), followed by dung (94%). Coal and dung also demonstrated the highest numbers and concentrations of PAHs. While dry applewood emitted ten times lower organic matter compared to ambient applewood, a higher fraction of these organics was composed of PAHs, especially the more toxic ones such as benzo(a)pyrene (9.63 ng/L versus 0.04 ng/L), and benzo(b)fluoranthene (31.32 ng/L versus 0.19 ng/L). Data from the AMS demonstrated no clear trends for any of the combustion fuels over the different combustion phases unlike the previously reported trends observed for the physical characteristics. Of the solid fuels, pellets demonstrated the lowest emissions. Emissions from propane were below the quantification limit of the instruments. This work highlights the benefits of incorporating additional metrics into the cookstove evaluation process, thus enriching the existing PM data inventory.

1. Introduction

The prominence of residential solid fuel combustion and its subsequent impact on both health and the environment has been well established (Chafe et al., 2014; Legros et al., 2009). Inefficient combustion in cookstoves generates products of incomplete combustion (PICs), leading to the formation of gases such as CO, SO_x, NO_x and volatile organic compounds (VOCs), and also of particulate matter (PM) – composed of elemental carbon, complex mixtures of organic matter, sulfates, nitrates, ammonium, and metals. Recent estimates put global annual mortality rates from household air pollution as a direct result from burning solid fuels in cookstoves at over 4 million, (Lim et al., 2012; Forouzanfar et al., 2017), making it the single most important environmental risk factor (WHO, 2017). What is more, the contribution of particulates to radiative forcing and cloud condensation nuclei (CCN) remains one of the largest uncertainties in global climate predictions (IPCC, 2013).

Studies have assessed PM emissions from cookstoves in both field (Leavey et al., 2015; Sahu et al., 2011; Commodore et al., 2013; Chengappa et al., 2007; Patel et al., 2017; Clark et al., 2010; Shan et al., 2014) and laboratory settings (Roden et al., 2009; Jetter and Kariher, 2009), with aerosol of aerodynamic diameter < 2.5 μm ($PM_{2.5}$) being the commonly accepted metric for quantifying particulate pollution. However, cookstove data with improved chemical speciation are needed to gain a better understanding of organic cookstove emissions and hence to constructively link specific compounds with specific disease outcomes, or environmental impacts. Although a handful of studies have used an Aerosol Mass Spectrometer (AMS) to characterize the bulk chemical composition of organic and inorganic non-refractory PM from residential wood combustion (Heringa et al., 2012; Kortelainen et al.,

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2015; Poulain et al., 2011; Schneider et al., 2006), few have done so while comparing multiple real-world relevant fuels. Additionally, previous studies have not explored how PM composition changes with different cookstove combustion phases, an important omission given the increasing onus on determining exactly which chemical compounds within this complex mixture are most deleterious to health, and at which point during cookstove operation, they are most frequently produced. The evidence is mixed regarding the importance of sulfate and nitrate-containing particles on human health risks (Atkinson et al., 2014; Lippmann and Thurston, 1995; Reiss et al., 2007; Lelieveld et al., 2015), therefore they should be included in any comprehensive measurement study.

Polycyclic aromatic hydrocarbons (PAHs) comprise a subset of organic species formed during pyrolysis or inefficient combustion of organic material. PAHs are relatively stable organic compounds containing carbon and hydrogen, and consist of 2 or more fused aromatic rings (IARC, 2010). PAHs can exist in both gaseous and particulate phases depending on their volatility and ambient conditions. While PAHs with a lower molecular weight (small PAHs, SPAHs) (e.g., naphthalene), are more volatile and tend to partition into the gas phase, the heavier PAHs (large PAHs, LPAHs) (e.g., benzo[*a*]pyrene) exist primarily in particulate form and are generally considered of greater concern to human health (IARC, 2010). Many PAHs and their metabolites are classed as carcinogenic, probably carcinogenic, or possibly carcinogenic to humans, as well as teratogenic and mutagenic (ATSDR, 2015; WHO, 2010; Kim et al., 2013; Ravindra et al., 2008). Human health effects from long-term exposure to PAHs include lung and bladder cancer, as well as cataracts, liver damage, and neural tube defects (Kim et al., 2013; Reid et al., 2012; Wang et al., 2014). Wang et al., (2008) were able to correlate ambient PAHs with cooking events, demonstrating that cookstove emissions are an important source of PAHs in both indoor and outdoor air.

Multiple laboratory and field studies have examined PAH concentrations emitted during coal (Chen et al., 2015; Huang et al., 2013; Ross et al., 2011; Wang et al., 2009; Russell, 2013), biomass (Wang et al., 2008; Boleij et al., 1989; Bruns et al., 2015; Li et al., 2011; Taylor and Nakai, 2012), plastic waste combustion (Greenbaum, 2013), or various combinations (but not all) of these fuels, as well as liquefied petroleum gas (LPG) (Ansari et al., 2010; Bhargava et al., 2004; Lisouza et al., 2011; Oanh et al., 2005, 1999; Raiyani et al., 1993a). However, few studies have compared PAH concentrations from an on-line instrument for the most widely used solid fuels (biomass, dung, and coal), and fewer still have examined chemically-speciated PAHs from an improved cookstove (ICS). Addressing this knowledge gap is important given the increasing onus on ICS distribution throughout the developing world which has seen more than 350 organizations from across the globe join together with the target of distributing ICS to 100 million households by 2020 (Bielecki and Wingenbach, 2014; GACC 04.12.17). Although switching to an ICS can significantly reduce the exposure to PICs including PAHs (Li et al., 2011), studies show that PM concentrations can remain dangerously high (Li et al., 2011; Patel et al., 2016a). Cookstove use, and the distribution of improved cookstoves, is set to continue. Moreover, while the majority of ICS manufacturers recommend pellets as the preferable solid fuel, few studies have characterized the chemical composition of PM emitted from pellets, making it difficult to draw meaningful comparisons with other commonly used fuels. It is important to empirically determine that as a household moves up the energy ladder, the members of that household are indeed decreasing their exposures to these harmful PICs. This study will therefore present normalized concentrations of PM, total organics, chloride (Cl^-), ammonium (NH_4^+), nitrate (NO_3^-) and sulfate (SO_4^{2-}), as well as particle-bound PAHs, from different solid fuels burned in a Phillips ICS during different cookstove combustion phases. The aim of this work is to increase our understanding of which chemical compounds are emitted under particular cookstove operation conditions, and to examine whether more metrics are needed to assess air quality in

indoor environments where cookstoves are frequently operated.

2. Methods

2.1. Cookstove and fuels

A forced-draft gasifier cookstove, Phillips (Model HD4012 LS), was selected for this study owing to its low emissions of $PM_{2.5}$ and black carbon (BC) reported in previous literature (Jetter and Kariher, 2009; Kar et al., 2012). A gasifier stove works as a dual-stage combustor. In the first stage, fuel gasifies to produce combustible gases and volatiles, which are oxidized in the second stage, producing a flame. More details about the operating principles of gasifier stoves can be found in Patel et al. (2016a). Four fuels corresponding to different rungs on the energy ladder were studied: (1) applewood chips, ambient (~6% moisture), and dry (~1%), (2) oakwood pellets, (3) cow-dung cakes (dung) and (4) coal. The high intra-variability between fuel types has been well-documented in the literature (Williams et al., 2012); however the focus of this study was to examine the inter-variability between fuel types and it is assumed that different woods etc., that are comprised of varying ratios of similar materials for example lignin and cellulose, will have more in common with each other than with other solid fuels. Likewise, the results presented are from a single type of cookstove. It is beyond the scope of this study to comment on the reproducibility of the results for other cookstoves and fuel combinations. Although biomass remains the most popular residential solid fuel, coal and dung use are not insignificant in China and India, respectively (Duan et al., 2014; Ministry of Home Affairs, 2015). For this study, dung was collected from grass-fed cows at a farm in Eureka, Missouri. Bituminous coal was procured from Brilliant, Alabama. Applewood chips, purchased locally and with no additives, were used as a proxy for fuelwood. Some of the applewood (dry applewood) was dried in an oven at 110 °C for 24 h (with a 4.9% weight loss), to assess the effect of moisture content on emissions. Commercially available propane, a cleaner fuel alternative similar in composition to LPG, which is the most common residential cooking fuel in urban India (Ministry of Home Affairs, 2015), was also tested using a single burner stove. None of the instruments detected any measurable species and so no further discussion on propane is included.

The Philips cookstove was operated according to the top-lit ignition method which requires that fuel be fed to the cookstove as a single-batch, followed by ignition at the top of the bed. For each experiment (coal excluded) 10 ml of ethanol was uniformly poured over the fuel to facilitate ignition. Because coal was difficult to ignite, 30 g of applewood was soaked in 20 ml of ethanol and added to the top of the coal bed for ignition. Similar to Patel et al., (2016a), the burn-cycle in the Philips was categorized into 3 phases. The start-up (SU) phase begins just after ignition, and is categorized by non-uniform flickering flames, which continues until the flame becomes steady, marking the start of the steady-state (SS) phase. After a period of stability, flames begin to weaken and eventually diminish as the extinguishing (Ext) phase sets in. Both the start time and the duration of each phase depend on the quantity of fuel fed to the cookstove. Table 1 presents the fuel loadings and approximate duration of the 3 phases of the burn cycle. Nine sets of

Table 1
The weights of the different fuels burned and durations of each phase of the burn-cycle.

Fuel type	Fuel weight (g)	Duration of the phase (minutes from ignition)		
		Start-up (SU)	Steady-state (SS)	Extinguishing (Ext)
Oakwood pellets	770	0–6	6–30	30-end
Applewood	260	0–4	4–10	10-end
Dry applewood	240	0–3	3–8	8-end
Cow-dung cakes	170	0–3	3–7	7-end
Coal	560	0–13	13–35	35-end