

Chemical characterization and toxicity of particulate matter emissions from roadside trash combustion in urban India

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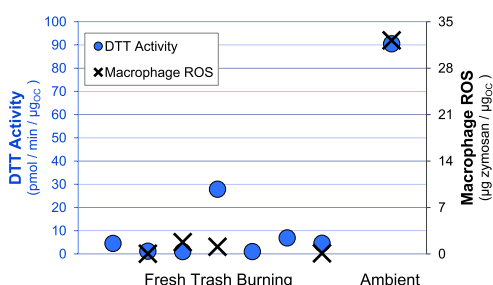
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HIGHLIGHTS

- PM_{2.5} samples were collected from 24 trash-burning piles in Bangalore, India.
- ROS activity of the collected samples was assessed by macrophage and DTT assays.
- Near source, exposure to redox-active PM is expected to be extremely high.
- Ambient PM_{2.5} indicates higher intrinsic ROS activity than fresh emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

Roadside trash burning is largely unexamined as a factor that influences air quality, radiative forcing, and human health even though it is ubiquitously practiced across many global regions, including throughout India. The objective of this research is to examine characteristics and redox activity of fine particulate matter (PM_{2.5}) associated with roadside trash burning in Bangalore, India. Emissions from smoldering and flaming roadside trash piles ($n = 24$) were analyzed for organic and elemental carbon (OC/EC), brown carbon (BrC), and toxicity (i.e. redox activity, measured via the dithiothreitol “DTT” assay). A subset of samples ($n = 8$) were further assessed for toxicity by a cellular assay (macrophage assay) and also analyzed for trace organic compounds. Results show high variability of chemical composition and toxicity between trash-burning emissions, and characteristic differences from ambient samples. OC/EC ratios for trash-burning emissions range from 0.8 to 1500, while ambient OC/EC ratios were observed at 5.4 ± 1.8 . Trace organic compound analyses indicate that emissions from trash-burning piles were

Abbreviations: BrC, brown carbon; CO, carbon monoxide; DTT, dithiothreitol; DTT_{OC}, OC-normalized DTT activity; DTT_V, volume-normalized DTT activity; EC, elemental carbon; GC-MS, gas chromatography mass spectrometry; LMICs, lower-middle income countries; NO_x, nitrous oxides; OC, organic carbon; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PM, particulate matter ($<2.5 \mu\text{m}$ in diameter); POA, primary organic aerosols; PVC, polyvinyl chloride; ROS, reactive oxygen species; SOA, secondary organic aerosols; VOCs, volatile organic compounds.

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DTT assay
Redox activity

frequently composed of aromatic di-acids (likely from burning plastics) and levoglucosan (an indicator of biomass burning), while the ambient sample showed high response from alkanes indicating notable representation from vehicular exhaust. Volume-normalized DTT results (i.e., redox activity normalized by the volume of air pulled through the filter during sampling) were, unsurprisingly, extremely elevated in all trash-burning samples. Interestingly, DTT results suggest that on a per-mass basis, fresh trash-burning emissions are an order of magnitude less redox-active than ambient air (13.4 ± 14.8 pmol/min/ μgOC for trash burning; 107 ± 25 pmol/min/ μgOC for ambient). However, overall results indicate that near trash-burning sources, exposure to redox-active PM can be extremely high.

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1. Introduction

Trash incineration is a global practice. Of the nearly 2 billion tonnes of garbage produced globally each year, possibly half is burned according to estimates by Christian et al. (2010) (Christian et al., 2010). In a 2012 report, the World Bank estimates that global costs associated with waste management will nearly double by 2025, disproportionately impacting lower middle income countries (LMICs), which are expected to see a 4-fold increase in waste management expenses (Hoornweg and Bhada-Tata, 2012). In addition to cost concerns, municipal waste services in many LMICs are limited, among other reasons, by their ability to confront steep population increases from rapid urbanization. In regions that lack access to consistent waste management services, it is common to encounter smoldering piles of garbage along the roadside or in open storm drains, often near residential areas. These trash piles are sources of air pollutants that include fine particulate matter ($\text{PM}_{2.5}$), volatile organic compounds (VOCs), nitrogen oxides (NO_x), and—due to incomplete combustion—carbon monoxide (CO) and polycyclic aromatic hydrocarbons (PAHs), many of which the International Agency for Research on Cancer (IARC) lists as probable carcinogens. Furthermore, trash burning may contribute to the formation of atmospheric brown clouds since studies have identified that other burning practices (e.g., agricultural burning, household biomass burning) are central contributors (Engling and Gelencser, 2010; Gustafsson et al., 2009).

Trash piles are intermittently burned to reduce accumulated waste and they are typically composed of paper products, food/plant matter, fabrics, plastics, and other waste. Plastic burning is of particular concern as it may produce toxic emissions that damage human health (Akovali, 2007; Junod, 1976). The combustion of chlorine-containing plastic (i.e., PVC) is known to generate dioxins and furans, especially under smoldering conditions (Lemieux et al., 2003), and release polychlorinated biphenyls (PCBs) (Costner, 2006; Hedman et al., 2005; Li et al., 2012; Shen et al., 2010), which bioaccumulate and do not readily degrade in the environment (Eisler, 1986a, b). Even though PCBs are persistent organic pollutants that have been targeted by the United Nations since the Stockholm Convention in 2001 (which India signed in 2002, then ratified in 2006), recent measurements collected by Chakraborty et al. (2013) in seven Indian cities show high atmospheric PCB concentrations; open waste burning is presumed to be a main contributor (Chakraborty et al., 2013). Significant HCl emissions have also been attributed to plastic waste burning (Christian et al., 2010; Li et al., 2012).

In general, open garbage burning emits high concentrations of $\text{PM}_{2.5}$ and predominately occurs in regions globally that already experience high ambient $\text{PM}_{2.5}$ concentrations. Recent studies estimate that over half of the Indian population lives in regions that exceed the annual Indian National Ambient Air Quality Standard of $40 \mu\text{g}/\text{m}^3$, and that 99.5% of the Indian population lives in regions

that do not meet the $10 \mu\text{g}/\text{m}^3$ WHO guideline (Dey et al., 2012; Greenstone et al., 2015). Garbage burning frequently occurs near people, including along traffic-heavy roadsides and residential areas, or at municipal dumpsites, which attract people who scavenge for recyclables to sell; the close proximity of emissions to people highlights the potential exposure and health implications of trash burning (Hodzic et al., 2012; Wiedinmyer et al., 2014). Previous studies have measured garbage-burning emissions in urban LMIC regions (Hodzic et al., 2012; Kumar et al., 2015; Lei et al., 2013; Li et al., 2012). Kumar et al. (2015) sampled municipal garbage-burning emissions from New Delhi landfill sites. In Mexico City, Hodzic et al. (2012) estimated that ~ half of all anthropogenic POA (primary organic aerosols) is generated by garbage burning; that study also estimated that mitigating garbage burning would result in a 2–40% decrease of organic aerosols and a 1–15% decrease in the city's $\text{PM}_{2.5}$ levels. Li et al. (2012) estimated that garbage burning in Mexico City contributes to 3–30% of $\text{PM}_{2.5}$ mass. However, data on roadside trash burning is limited.

This study provides a distribution of roadside garbage-burning characteristics measured from representative, real world events, and also makes the first ever measurements of toxicity. We employ assays that test for reactive oxygen species (ROS), which are known to cause inflammatory responses in cells (Simon et al., 2000). Other analyses include elemental and organic carbon (EC and OC), brown carbon (BrC), and organics, including alkanes, PAHs, di-acids, alkanic acids, and levoglucosan, providing new detail on the composition of the emissions.

2. Material and methods

2.1. Site descriptions

Sampling was conducted in and around Bangalore, India and emissions were drawn from roadside burning events encountered in the area (Fig. 1). All samples were collected in October 2013 during daytime hours (~9:00–16:00). The trash-burning piles ($n = 24$) varied in size, burning conditions, and material composition, although nearly all piles (23/24) contained notable amounts of plastic. The majority of piles exhibit smoldering and flaming conditions: ~83% (20/24) show smoldering and ~83% (20/24) show flaming, with ~67% (16/24) of trash piles simultaneously showing both smoldering and flaming. These burning conditions are visually evident in the documented site photographs and also analytically evident in the results from OC/EC analysis. Additional burn information and filter properties (Table 1) including filter color, burning conditions (smoldering and/or flaming), and burning material composition (e.g., plastic, paper, synthetics, etc.) were also qualitatively documented. The most common materials observed, in order of prevalence, are plastic, paper, biomass, cloth, foil, electronics/wires, rubber, and glass. Other interesting yet not recurring materials observed in burn piles include car seat upholstery and



Fig. 1. The locations of the trash-burning sampling sites ($n = 24$) are marked by gray pins. Thin pointer lines connect some pins to photographs taken at the sampling sites in order to show the variability of encountered trash-burning piles: S12 shows a small pile with smoldering and flaming conditions along a dirt road; S18 shows a large smoldering pile on a paved road; S17 shows an even larger smoldering pile near a bus station; S14 shows a small pile almost entirely comprised of smoldering plastic near a residential area.

tube lights. All ambient samples ($n = 6$) were collected at a remote site in Bangalore located away from observable primary emission sources (e.g., traffic, industry, burning practices).

2.2. Sampling & analyses

All samples ($n = 24$ trash burning; $n = 6$ ambient) were collected on 37-mm quartz filters using a $PM_{2.5}$ inertial impaction sampler (Personal Environmental Monitor) attached to a pump (Leland Legacy), which operated at a flow rate of 10 LPM. In order to minimize the influence of non-trash-burning sources, trash-burning samples were collected in close proximity to the pile. The sampling inlet was suspended ~ 0.5 m above the burn piles. This height between the sampling inlet and the burn pile varied slightly depending on burning conditions but was within a range of 0.3–1.0 m. Since the filters were rapidly loaded, total sampling time was brief (~ 2 –20 min). Ambient samples were collected over a duration of ~ 24 h and were also used for background subtraction of the trash-burning samples.

All filters were analyzed for organic and elemental carbon fractions (OC and EC), water- and methanol-soluble brown carbon (BrC), and toxicity in terms of oxidative potential. The potential for samples to generate ROS was assessed using the dithiothreitol (DTT) assay (methods described by Cho et al. (2005)), which measures the ability of PM to catalyze electron transfer from DTT to oxygen and form ROS; the rate of DTT loss (measured in nmol of DTT consumed per minute) is proportional to the amount of PM-generated ROS in the sample (Charrier and Anastasio, 2012; Cho et al., 2005; Delfino et al., 2013; Fang et al., 2015; Kumagai et al., 2002). OC and EC were measured with a Thermal Optical Transmittance Carbon Analyzer (Sunset Laboratory Inc.), following the NIOSH protocol (Birch, 1998; Watson et al., 2005). Light absorption of BrC was detected by a UV–Vis spectrometer (Ocean Optics) as water and methanol filter extracts were pulled through a Liquid Waveguide Capillary Cell (World Precision Instruments) (Hecobian

et al., 2010; Liu et al., 2013).

For a subset of samples ($n = 7$ trash burning; $n = 1$ ambient) Gas Chromatography – Mass Spectrometry (GC-MS) was used to assess filter solvent extracts for alkanes, PAHs, aromatic di-acids, alkanolic acids, and levoglucosan (Stone et al., 2008). These 8 samples were also analyzed for cellular ROS production using a rat alveolar macrophage assay (Landreman et al., 2008). For the GC-MS analysis, the 8 samples were spiked with labeled internal standards and then extracted with a mixed solvent of methylene chloride and acetone using sonication and were concentrated using a rotavap and nitrogen blow down. The concentrated samples were derivatized with diazomethane, and samples were then analyzed by GC-MS for n -alkanes, PAH, and hopanes, steranes, and organic acids. An aliquot of the sample was derivatized with trimethylsilylation reagent and this aliquot was analyzed by GC-MS in a separate analysis for levoglucosan as the trimethylsilyl ester. Multi-point calibration curves with authentic standards were used for quantification. Additional details for the analysis are presented by Stone et al. (2008). The cellular ROS assay was conducted by extracting the 8 samples in water and exposing the extracts to NR8383 rat alveolar cells proliferated from a commercial cell line. The cells were exposed to the extract for 2.5 h at 37 °C, and the cellular ROS production was measured with a DCFH probe. Cell passage numbers did not impact assay results once normalized to positive controls and therefore was not quantified for each assay. Additional details for the assay are presented by Landreman et al. (2008) (Landreman et al., 2008).

3. Results and discussion

3.1. PM general carbonaceous properties

Trash-burning and ambient filter carbonaceous analyses are summarized in Table 2. Results show a wide distribution of emissions characteristics for the trash-burning piles. Even piles of

Table 1

Visual properties of trash-burning samples ($n = 24$) are listed in order of increasing OC/EC ratios. Visual properties include filter photographs (first column), burning conditions, and material composition.

Filter Color/ID	OC/EC	Burning condition	Burning material composition
● S 01	1	Large flames	Paper (majority), plastic, electrical wiring/coil
● S 02	14	Dense sooty smoke + flames	Plastic, paper, canvas shoes, green waste
● S 03	16	Dense smoldering + large flames	Paper (majority), plastic, tube lights
● S 04	27	Smoldering + small flame	Timber waste (majority), plastic
● S 05	31	Smoldering + flames	Paper, plastic
● S 06	40	Dense sooty smoke + flames	Plastic, paper
● S 07	44	Smoldering + large flames (briefly)	Paper (majority), plastic, aluminum foil
● S 08	46	Dense smoldering + small flame	Synthetic/cotton cloth
● S 09	47	Smoldering + flames	Plastic (majority), rubber, cotton, expanded polystyrene (Thermocol), paper
● S 10	88	Smoldering + small flame	Paper, green waste (banana stalk), aluminum foil, plastic
● S 11	106	Smoldering + small flame	Newspaper (majority), plastic, leaf litter
● S 12	107	Smoldering + small flame	Plastic, green waste, paper
● S 13	117	Smoldering + large flames	Newspaper (majority), cartons, plastic, green waste
● S 14	133	Small flames	Tetra Pak ^a (majority), paper, plastic
● S 15	261	Smoldering + very small flames	Plastic, paper, aluminum foil, coconut shell
● S 16	291	Smoldering + small flames (briefly)	Paper (majority), plastic, cotton cloth
● S 17	339	Smoldering + small flame	Tetra Pak ^a (majority), green waste, plastic
● S 18	400	Smoldering + flames	Paper (majority), plastic, aluminum foil, green waste, cotton cloth
● S 19	488	Smoldering + small flame	Leaf litter (majority), plastic, paper, green waste
● S 20	942	Smoldering + small flame	Paper, plastic, green waste
● S 21	–	Smoldering	Paper (majority), plastic
● S 22	–	Smoldering	Synthetic rug (majority), plastic, electrical components, green waste, glass
● S 23	985	Smoldering	Plastic (majority), car upholstery, paper, green waste
● S 24	1536	Smoldering	Plastic, paper, aluminum foil, coconut shell

^a Tetra Pak packaging is made of paperboard, polyethylene, and aluminum.

similar size, composition, and smoldering/flaming conditions are observed to produce vastly different emissions concentrations.

As mentioned previously, nearly all of the trash-burning piles were observed to be smoldering. Smoldering combustion, which typically occurs at lower temperatures than flaming combustion (Ohlemiller, 1985; Rein, 2009), tends to produce high levels of organic carbon (Reid, 2005) and, as anticipated, very high OC mass concentrations are observed in the burn piles since measurements occurred near-source, directly in the exhaust plume. OC mass concentrations range from ~13,000 to 462,000 $\mu\text{g}/\text{m}^3$ (interquartile range: ~88,000–136,000 $\mu\text{g}/\text{m}^3$). Observed EC results (which range from ~100 to 16,000 $\mu\text{g}/\text{m}^3$) display the expected affiliation between flaming conditions and elevated levels of elemental carbon (Reid, 2005). Unsurprisingly, the highest EC mass concentration is

observed in the pile with largest visible flaming fraction. Furthermore, the trash piles that did not exhibit flaming conditions produce EC concentrations below the interquartile range (~360–2500 $\mu\text{g}/\text{m}^3$); measured EC concentrations for non-flaming trash samples are not observed to exceed 250 $\mu\text{g}/\text{m}^3$. OC/EC ratios from trash burning are highly variable. Ratios range from less than 1 to greater than 1500 (interquartile range: ~40–330). This range is significantly higher than ambient OC/EC ratios (5.4 ± 1.8). A study by Kumar et al. (2015) that examined smoldering dumpsites in New Delhi, India measured OC/EC ratios of 43 ± 2 (Kumar et al., 2015). The lower OC/EC ratios are assumed to predominately be attributed to increased dilution with ambient air; unlike our study, which sampled ~0.5 m from the source, Kumar et al. (2015) sampled ~2.5 m above ground level, permitting increased levels of mixing

Table 2

Carbonaceous species in trash burning and ambient $\text{PM}_{2.5}$. Organic carbon (OC) and elemental carbon (EC) mass concentrations are shown in units of $\mu\text{g m}^{-3}$ and light absorption from water- and methanol-soluble brown carbon (BrC) is in units of $\text{Mm}^{-1}\mu\text{gOC}^{-1}$ (i.e., inverse megameters normalized to μg of OC mass).

	Trash burning ($n = 24$)					Ambient ($n = 6$)				
	Mean	Min	Max	S.D.	Quartiles	Mean	Min	Max	S.D.	Quartiles
OC/EC	275	0.80	1537	396	41–327	5.44	3.08	8.05	1.81	4.32–6.38
OC	125,000	13,000	462,000	91,000	88,000–136,000	7.50	6.62	9.28	0.96	6.88–7.57
EC	2444	87	16,436	3728	362–2506	1.53	0.84	2.15	0.55	1.15–1.99
BrC-MeOH/OC	3.98	0.66	8.99	2.10	2.66–4.59	0.039	0.004	0.056	0.019	0.035–0.052
BrC-H ₂ O/OC	3.46	0.18	9.07	2.47	1.56–4.85	0.028	0.020	0.036	0.006	0.026–0.033

with ambient air (ambient air has lower OC/EC ratios than fresh trash-burning emissions). Both studies signify substantial OC contributions from extended low temperature smoldering conditions.

Smoldering biomass burning also produces considerable amounts of brown carbon (BrC) (Chakrabarty et al., 2010; Hoffer et al., 2006; Kirchstetter, 2004; Lack et al., 2013). The BrC measurements shown in Table 2 are divided by OC mass in order to normalize the varied sampling times and loadings of the trash-burning and ambient filters. As mentioned by Yang et al. (2009), dividing by OC will underestimate BrC (as OC mass does not account for all light scattering and absorption), but OC-normalized BrC is useful in facilitating comparisons for different loadings (Yang et al., 2009). Even though the OC loadings on the trash-burning filters were extremely high, the OC-normalized BrC measurements are still more than 100 times higher than ambient light absorption, indicating that trash-burning emissions may become less brown as they are aged and processed in the atmosphere. BrC light absorption in the trash-burning filters was expected to vary considerably since smoldering typically generates light-colored smoke while flaming conditions may produce black sooty smoke. On average, methanol-soluble BrC reports slightly higher absorption values than water-soluble BrC for both trash-burning and ambient samples. This is expected since, compared to water, methanol permits higher dissolution of non-polar compounds. Trash-burning filters are diverse in color (see Table 1), demonstrating shades of brown, gray, pale yellow, orange, and black. The colored circles displayed in Table 1 are cropped from actual images of each filter (all photographed under identical lighting conditions). When sorted according to OC/EC ratios, a clear gradient emerges from lighter colored filters (high in OC) to very black filters (high in EC). No other explicit implications relating filter color and other measured components were observed in this sample set.

3.2. Trace organic composition of PM

The distributions of trace organics for a subset of trash-burning and ambient samples ($n = 7$ and $n = 1$, respectively) are shown in Fig. 2. Results are shown per organic mass (OM) using an OM/OC factor of 1.8 (Gilardoni et al., 2009; Reid, 2005). The trash-burning samples display organic compositions that are significantly different from the ambient sample. This finding is expected because many sources contribute to ambient concentrations, with no one source dominating. Previous studies (Chakraborty and Gupta, 2010;

Chowdhury et al., 2007; Pant et al., 2015; Patil et al., 2013) of atmospheric particulate matter in India have documented significant contributions from vehicle exhaust, road dust, biomass burning, coal combustion, and SOA (Bhattu and Tripathi, 2015; Fu et al., 2010; Rengarajan et al., 2011). However, robust information about source apportionment is lacking for India (Pant and Harrison, 2012). The sources that dominate ambient concentrations may be more amenable to GC-MS analysis since there are likely many unresolved compounds that comprise considerable portions of the trash-burning samples; this is a possible explanation for the notably higher magnitude of trace organics observed in the ambient sample. The GC-MS quantified organic compounds make up 10–25% of the measured organic mass in the emissions samples, which is consistent with previous measurements of particulate matter emissions from combustion sources (Schauer et al., 1999a, b; 2001), and results from the fact that many organic compounds in particulate matter emitted from combustion sources are not extracted or elutable and cannot be measured by standard GC-MS methods.

Results from the ambient analysis identify alkanes as the largest component of measured organics. The second-most common organic component for the ambient filter is alkanic acid, which is typically associated with primary biogenic sources (e.g., plants, cooking, road dust) (Heo et al., 2013). Alkanes and alkanic acids dominate composition of ambient samples, but are also present—to lesser extents—in trash-burning samples. Studies by Fu et al. (2009) and Alves et al. (2012) suggest that open waste burning emits long chain alkanes (Alves et al., 2012; Fu et al., 2010). Of all trash-burning samples analyzed for *n*-alkanes, 4 of 7 are observed to have *n*-chains that exceeded the highest *n*-chain in the ambient sample (C_{36}). Two of 7 trash-burning samples show carbon numbers of C_{40} , which has previously been observed in plastic burning experiments (Simoneit et al., 2005). The ambient sample shows responses for all *n*-alkanes between 28 and 36—ambient *n*-chains for $n > 25$ have been associated with unburned diesel and gasoline emissions (Rogge et al., 1993). This aspect may be contributing to the high *n*-alkane composition observed in the ambient sample because, as mentioned previously, traffic emissions are known to be a dominating source to ambient pollution. GC-MS responses differed between ambient and trash-burning samples but both appear in the same region of the carbon preference index (CPI).

For the trash-burning filters, 3 of 7 samples measure highest

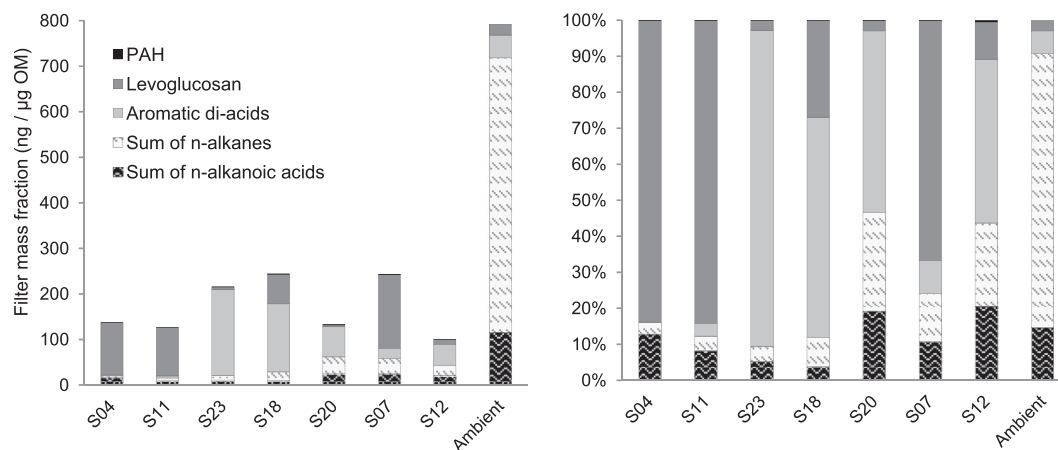


Fig. 2. Emissions composition based on GC-MS analysis (ng on filter per μg of total organic mass). Seven trash-burning filters (S04, S11, S23, S18, S20, S07, S12) and one ambient filter were analyzed. In order to observe both the magnitude and the composition of the GC-MS resolved organics, emissions are displayed in two ways: the first graph (left-side) shows nanograms of organic compound per micrograms of total organic mass (OM), and the second (right-side) shows a 100% stacked distribution.

emissions rates for levoglucosan, which is the only sugar selected for GC-MS analysis and is also an indicator of biomass burning (Schauer et al., 2001). The burn piles for these 3 levoglucosan-majority samples were, unsurprisingly, primarily composed of paper and biomass. As mentioned previously, smoldering biomass burning generates significant amounts of BrC. Related to this aspect, levoglucosan displays a remarkable correlation with water- and methanol-soluble BrC ($R^2 = 0.96$ and $R^2 = 0.83$, respectively). Because of the small sample size of the dataset ($n = 7$), this observed correlation should be taken with caution.

Four of 7 trash-burning filters show aromatic dicarboxylic acids (di-acids) to be the dominating component of resolved organic carbon mass. Di-acids are generally dominated by secondary formation and are a part of SOA, which is likely the reason for the notable presence of di-acids in the ambient fraction (Schauer et al., 1996). But di-acids may also be primary (Chebbi and Carlier, 1996), as seen in these trash-burning samples where di-acids are the major component. Measured di-acids include terephthalic and isophthalic acid. Di-acids are commonly identified in plastic-burning mixtures (Kumar et al., 2015). Among the samples analyzed for di-acids, S23 shows the highest levels of total di-acids. Site records noted a visibly higher plastic composition in the S23 burn pile compared to other sampling sites measured by GC-MS. This notable prevalence of plastics is likely responsible for the high di-acid concentration, since previous studies have found that plastic burning produces terephthalic acid emissions (Simoneit et al., 2005). The S04 site, which reports the lowest di-acid concentration of the tested samples, is the only burn pile that was primarily composed of biomass (other piles were dominated by plastic or paper).

Since PAHs are a comparatively smaller portion of the organic mass fraction, Fig. 3 shows a closer look at the distributions. The first graph (left-side) proportionally displays PAH mass fractions (ng of PAHs on the filter per μg of total organic mass) while the second graph (right-side) displays the same data in 100% stacked distributions so that the components of each organic are clearly visible. Note that the figure does not display all measured PAHs, and excludes very volatile PAHs that are present in both the gas and particle phase such as fluoranthene, pyrene, and retene. A table listing all PAH mass fractions can be referenced in the Supporting Information (Table S1). GC-MS analysis did not measure detectable levels of ambient PAH components as the OC collected on the ambient samples was relatively small and did not provide large enough organic mass for low detection limits for the ambient samples. The selected PAHs are found in wood preservatives, dyes,

and burning tars or biomass materials; they are also all associated with genotoxicity and most are probable carcinogens (WHO). Trash-burning sample S12 shows the highest emissions rate of PAHs, with 2–35 times more PAHs per μg of organic matter than the other tested samples (2.5–65 times more PAHs per volume). This sample is also the only one that shows a measurable level for Benzo(j)fluoranthene. S12 also produced the highest EC mass concentrations of the tested GC-MS samples but no correlation between EC and PAH concentration is observed over the sample set.

3.3. Toxicity (redox activity)

Results from ROS analyses are listed in Table 3; water-soluble DTT consumption rates are normalized per OC mass (DTT_{OC}), as well as per unit volume of sampled air (DTT_V). There are no comparable DTT_V reference values for trash burning, but ambient values (measured in urban areas) have reported typical DTT consumption rates between ~ 0.2 – 0.8 nmol/min/ m^3 (Charrier and Anastasio, 2012; Cho et al., 2005; Fang et al., 2015; Hu et al., 2008; Ntziachristos et al., 2007; Verma et al., 2009b). Cho et al. (2005) measured one urban ambient sample as high as ~ 1.3 nmol/min/ m^3 . Our DTT_V analyses report ambient samples ranging between 0.66 and 1.03 nmol/min/ m^3 , while the trash-burning filters, on average, show DTT consumption rates exceeding 1000 nmol/min/ m^3 . Additionally, previous studies have indicated that particle-phase semivolatiles play a major role in DTT activity (Biswas et al., 2009; Verma et al., 2011), so measured DTT activity may be underestimated due to high temperature sampling forcing semi-volatile species from collected particles into the gas phase. These high DTT_V levels clearly indicate unhealthy conditions for people passing by roadside burn piles or living in near-source regions; although, given the close proximity of the sampling line to the burn pile, it is not surprising that trash-burning DTT_V consumption rates are extremely high. Interestingly, on a per-OC mass basis, the trash-burning filters show lower DTT consumption rates than the ambient filters, implying that trash burning produces many non-redox-active compounds. Ambient DTT_{OC} is ~ 2 – 100 times higher than trash-burning DTT_{OC} . This substantial difference in redox activities suggests that the particulate matter in ambient air is, on a per-mass basis, intrinsically more toxic (i.e., more redox-active) than fresh trash-burning emissions. This finding may indicate that the transformation and aging of aerosols in the atmosphere results in increases in redox activity—an idea that has been proposed by other recent studies (Antinolo et al., 2015; Li et al., 2009; McWhinney et al., 2011; Rattanavaraha et al., 2011; Stevanovic

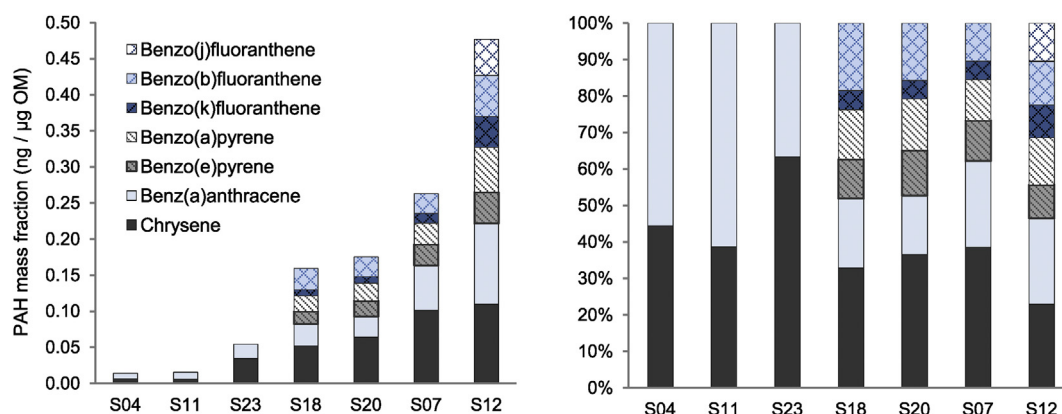


Fig. 3. Distributions of selected PAHs in seven trash samples (S04, S11, S23, S18, S20, S07, S12; shown in order of lowest PAH mass fraction to highest). In order to observe both the magnitude and the composition of the PAH distributions, emissions are displayed in two ways: the first graph (left-side) shows nanograms of PAHs per micrograms of organic mass, and the second (right-side) shows a 100% stacked distribution of the selected PAHs.

Table 3

ROS analyses for trash burning ($n = 24$; “S01–S24”) and ambient filters ($n = 6$; “A1–A6”). Units for DTT consumption rate per volume (DTTV) are nmol/min/m³ and units for DTT consumption rates per μg of OC mass (DTTOC) are pmol/min/ μgOC . Macrophage assay results are normalized to OC and expressed in equivalent activity of the positive control Zymosan, with the standard deviation of replicated measurements presented in parentheses.

Filter ID	DTTV	DTTOC	Macrophage/OC
S 01	895	68.2	–
S 02	776	6.4	–
S 03	624	14.7	–
S 04	98	1.0	1.77 (0.20)
S 05	869	7.4	–
S 06	610	7.0	–
S 07	105	1.2	0.03 (0.04) ^a
S 08	3220	32.0	–
S 09	518	10.5	–
S 10	1000	5.9	–
S 11	1610	27.9	1.08 (0.36)
S 12	3190	7.0	–0.12 (0.05)
S 13	1660	13.8	–
S 14	1700	12.4	–
S 15	1190	12.4	–
S 16	955	14.4	–
S 17	3510	25.0	–
S 18	130	1.0	–0.03 (0.03) ^a
S 19	1880	10.7	–
S 20	402	4.5	–0.43 (0.14) ^a
S 21	89	–	–
S 22	391	–	–
S 23	1130	4.6	0.09 (0.04)
S 24	1000	7.5	–
A 1	0.79	103.0	–
A 2	0.76	81.4	–
A 3	1.03	152.8	–
A 4	0.75	113.7	–
A 5	0.66	90.5	32.19 (6.0)
A 6	0.75	101.3	–

^a Extract was toxic to macrophage cells as implied by increase in biological activity and decrease in extract concentration.

et al., 2013; Verma et al., 2009a, 2014, 2015a, 2015c). Those studies measured increased redox activity for oxygenated aerosols (i.e., particles subjected to photochemical aging, ozone oxidation, etc.). A summary of studies that indicate that oxidative aging plays a major role in increasing redox activity is summarized by Verma et al. (2015b). The higher mass-normalized DTT response (DTTOC) observed in the ambient samples suggests that trash/refuse burning is not a significant fraction of ambient PM, or possibly—as just mentioned—that primary trash-burning emissions become more redox active as they are processed and aged in the atmosphere. We are not, however, suggesting that fresh trash-burning emissions are any more or less hazardous to human health than other PM emission sources. The extremely elevated DTTV responses generated by the trash-burning samples suggest that close proximity to burning piles would result in high levels of exposure to ROS-generating PM given the immense concentrations emitted near burning activities.

Since results are only indicative of water-soluble DTT activity—and the compounds present in trash burning are not all water-soluble—some trash-burning and ambient samples ($n = 7$ and $n = 1$, respectively) were also assessed for methanol-soluble DTT activity. The methanol-soluble responses observed from this subset did not indicate any noteworthy comparisons nor did they show significant differences from the water-soluble results. Therefore, we expect the water-soluble DTT results to be a useful indicator of total DTT activity. Water-soluble DTT analysis was performed once per filter and the absolute error for trash-burning measurements was ~8% for each sample (for volume- and mass-normalized results). For the ambient filters ($n = 6$), average DTTV and DTTOC activities

measure 0.79 ± 0.13 nmol/min/m³ and 107 ± 25 pmol/min/ μgOC respectively.

As previously mentioned, a cellular assay (the macrophage assay) was used to further evaluate the redox activity of some ($n = 7$) trash-burning samples and one ambient sample. The use of rat lung cell macrophages innately provides more representative estimates of redox activity than a chemical assay like DTT—although DTT is less time-consuming. Also, the DTT assay has shown correlations with the macrophage assay in a previous study by Hu et al. (2008), suggesting that both assays are sensitive to similar compounds (Hu et al., 2008). We therefore anticipated the macrophage assay to produce responses that are comparable to the DTT results. The correlations between DTT and macrophage results do not exhibit a linear relationship, but they show similarity in responses between ambient and trash-burning samples.

As with DTTOC analysis, the macrophage analysis normalized to OC mass shows a much higher redox activity for the ambient sample than for the trash-burning samples. This finding further suggests that fresh trash-burning emissions are less redox active on a per-mass basis than ambient PM_{2.5}. Results (Table 3) show that 3 of 7 trash-burning samples produced negative results. This behavior is attributed to the occurrence of cytotoxicity (i.e., cell membrane leakage, which can be detected by the lactate dehydrogenase assay (Landreman et al., 2008; Okayama et al., 2006)) suggesting that trash-burning emissions were toxic to the macrophage cells. All three of the samples tested for cytotoxicity (S07, S18, S20) confirmed that cell leakage was present, signifying that the sample extract made the cells sick. It is recommended for future research to assess toxicity of additional pathways to increase understanding of how trash-burning emissions affect cells.

Another relevant factor is that the DTT assay is not sensitive to all organic compounds present in trash burning, so the oxidative potential (as measured by DTT activity) may underestimate the generation of ROS that would actually occur in human cells. If an OC compound would generate a response in the body but does not produce a response to DTT, then normalizing by total OC mass would make the redox response appear artificially low. However, the DTT assay is responsive to many of the compounds observed in trash burning, and since the differing responses from ambient and trash-burning samples are prominent in both chemical and biological assays, we do not expect the impact due to sensitivity limitations of the DTT assay to have significantly altered the findings.

A previous study by Ntziachristos et al. (2007) suggests that PAHs correlate to DTT activity (PAHs do not directly generate ROS) by oxidizing into quinones or semi-quinone radicals, which may then generate ROS (Ntziachristos et al., 2007). However, this response is not explicit in our measured samples as no correlation is observed between PAH levels and DTT activity, suggesting that the PAHs alone do not capture most of the DTT activity. In fact, there are no unequivocally observable correlations between redox activity and other analyses. This is not surprising as the composition of trash-burning piles varies extensively. Moving forward, assessing redox activity of trash burning could be improved by knowing the isolated responses of plastic burning on the DTT and macrophage assays, since plastic is the most common material being burned. Knowing the responses from both assays would allow for better comparison between DTT and macrophage results.

3.4. Conclusions

In summary, ROS results measured using both the DTT and macrophage assays find that on a per-mass basis, fresh trash-burning emissions appear to be less redox active than the PM_{2.5} in ambient air. Our analyses also find that volume-normalized trash-burning emissions, unsurprisingly, generate considerably

higher redox activity than ambient air. On this per-volume basis, the ambient background average (0.79 ± 0.13 nmol/min/m³) is significantly lower than trash-burning DTT_v consumption rates, taken from in-plume measurements, which range from ~100 to 3500 nmol/min/m³. In fact, results suggest that ~1 min of direct exposure to trash-burning emissions (i.e., if a person were directly breathing from within the plume, only 0.5 m from the combustion itself—this is unrealistic but a useful thought experiment) is equivalent (in DTT_v activity) to an entire day of breathing in ambient air. Compositional analyses of trash-burning filters highlight a broad distribution of OC/EC ratios and vastly different fingerprints of organics, including plastic burning signatures. The prevalence of trash burning in India and elsewhere, along with these results on the composition and oxidative activity of actual, in situ, trash-burning emissions provide additional evidence that trash burning represents a significant public health hazard. Further, recent findings on the soiling of the Taj Mahal give added impetus to identifying potential controls (Bergin et al., 2015).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.09.041>.

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