



Understanding the Influence of Open-waste Burning on Urban Aerosols using Metal Tracers and Lead Isotopic Composition

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ABSTRACT

Open-waste burning (OWB) is one of the primary sources of urban aerosols in several developing countries. To better understand the influence of OWB emissions on urban aerosols, total suspended particles (TSP) and size-segregated samples were collected at an open-waste burning site (the Okhla landfill) and two urban sites in New Delhi. The TSP samples were analysed for selected metals (As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) using ICP-MS. In general, among the metals, Fe and Zn were mostly dominant, and As, Cd and Se were found in trace concentrations in the majority of the samples. Additionally, Pb concentrations were ~5–8 fold higher in urban wintertime samples than other samples. Tin, a tracer for waste-burning aerosols, ranged between 0.055 and 0.675 $\mu\text{g m}^{-3}$ in OWB aerosols. Interestingly, the concentration of Sn was significantly high in the urban wintertime aerosols, specifically, 0.082–0.284 $\mu\text{g m}^{-3}$. Tin also showed a high enrichment factor in the urban wintertime aerosols, suggesting its anthropogenic origin, possibly because of enhanced OWB practices in winter. Waste burning was also found to be one of the primary sources of chromium, which ranged between 0.102 and 0.606 $\mu\text{g m}^{-3}$ in OWB aerosols and between 0.114 and 0.574 $\mu\text{g m}^{-3}$ in urban aerosols. Since Cr(VI) is of interest due to its impact on health, the soluble Cr(VI) concentration was determined and found to be 6.12–10.2 ng m^{-3} (~1–6% of the total Cr in OWB aerosols compared to 0.33–0.65 ng m^{-3} [$< 1\%$ of the total Cr]) in urban aerosols. The lead isotopic signatures of OWB aerosols, viz., the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, were determined to be 2.1309 ± 0.0029 and 1.1316 ± 0.0035 , whereas those of the urban aerosols were 2.1369 ± 0.0026 and 1.1243 ± 0.0024 , respectively. However, the ranges of these values among the different aerosol types were not very distinct and showed discreet overlaps. This Pb isotopic study, along with metal fingerprints, suggests the increased influence of OWB emissions in winter on New Delhi aerosols.

Keywords: Open waste burning emissions; Metal signatures; Chromium(VI); Lead isotope.

INTRODUCTION

Urban aerosols are a mixture of several species which contribute from a wide array of sources. Many of these sources are identified and characterized well. However, the fast changing lifestyle and land-use patterns add new sources of emissions. The increasing usages of packaged products have led to an increase in production of waste, which seems to increase further in future. The general way to minimize

household waste is to burn it or to dump it in landfills (Kassim, 2006; Christian *et al.*, 2010; Wiedinmyer *et al.*, 2014; Kumar *et al.*, 2015). In developed countries, waste incinerators (controlled burning of waste to harness energy) and recycling plants work for waste management (Wiedinmyer *et al.*, 2014). However, in developing countries where waste collection efficiency is poor and waste to energy initiatives are low, majority of waste generated lands up in landfills or burns in nearby localities (Wiedinmyer *et al.*, 2014; Kumar *et al.*, 2015). This practice is termed as open waste burning (OWB).

Open waste burning generally refers to an uncontrolled burning of any waste including agricultural wastes and crop residues. However in urban context, it refers mainly

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to urban wastes comprising compostable materials (such as biomass including garden waste, paper, natural fabrics, and food materials from kitchen waste) and non-compostable materials including recyclables (mainly polythene/plastic materials, foam, packing and packaging materials, metals, etc.) and non-recyclables (thermosetting plastics and inert materials like construction and demolition waste, excavated soil, silt, etc.) which form the bulk (Christian *et al.*, 2010). Urban waste is specifically important as it contains a significant chunk of plastics, e-wastes and other high-tech wastes which on burning emits hazardous and toxic species (Gullett *et al.*, 2007; Christian *et al.*, 2010; Wäger *et al.*, 2011; Kumar *et al.*, 2015).

Open waste burning practices have been reported to be common in several parts on the globe including India, China, Mexico, Tanzania, Mongolia, etc. (Kassim, 2006; Christian *et al.*, 2010; Li *et al.*, 2014; Park *et al.*, 2013; Kumar *et al.*, 2015). Globally, it has been estimated that 2400 Tg of waste is generated annually out of which 970 Tg (41%) is burned openly at the residential area and at dump sites or landfills combined together (Wiedinmyer *et al.*, 2014). Open burning of wastes is known to produce particulate matter and other toxins like benzene, polyaromatic hydrocarbons (PAHs), metals, polychlorinated biphenyls, etc. (Christian *et al.*, 2010; Park *et al.*, 2013; Wiedinmyer *et al.*, 2014; Kumar *et al.*, 2015).

Emission of metals from waste burnings is evident in a few studies reported earlier (Christian *et al.*, 2010; Park *et al.*, 2013). Christian *et al.* (2010) proposed Sb as a tracer for OWB emissions in Mexico City. Another tracer, Sn, was proposed for plastic-enriched waste burning emissions for the New Delhi aerosols (Kumar *et al.*, 2015). Metal emissions from waste burnings are largely dependent on the composition of the waste materials. Although there are studies on the chemical compositions of waste burnings aerosols, very limited data on the chemical compositions of waste burning emission is available, especially from the Indian region (Kumar *et al.*, 2015).

Emission inventories have recently included the OWB as one of the sources of urban emissions (NEERI, 2010; Gargava *et al.*, 2014; Wiedinmyer *et al.*, 2014). However, the comprehensive understanding of this source is still missing, hence the estimation of emissions from the region may be underestimated (Wiedinmyer *et al.*, 2014). Emission inventory studies in India have also included OWB source recently (NEERI, 2010; Gargava *et al.*, 2014). But the contribution of OWB to the Delhi aerosols have been estimated to be non-significant (Gargava *et al.*, 2014), which is in contrast to the significant contributions reported from China, Mexico, etc. (Christian *et al.*, 2010; Wiedinmyer *et al.*, 2014). Further, to extend the scope of chemical compositional analyses, stable isotopic signatures may be very useful.

Isotopic signatures of the emission sources have been found to be useful to trace the sources of contaminants, and Pb isotopic ratios have been used widely in aerosol study (Bollhöfer and Rosman, 2001; Carignan *et al.*, 2005; Grousset and Biscaye, 2005; Geagea *et al.*, 2008; Komárek *et al.*, 2008; Kumar *et al.*, 2016; Sen *et al.*, 2016). However,

Pb isotopic data of aerosols and street dust from Indian region are scarce (Das *et al.*, 2016; Kumar *et al.*, 2016; Sen *et al.*, 2016; Das *et al.*, 2018). Kumar *et al.* (2016) reported Pb isotopic data of transported dust over New Delhi and urban aerosols. Also the paucity of sufficient Pb isotopic data for the end-member sources from the Indian region was observed (Das *et al.*, 2016; Kumar *et al.*, 2016; Sen *et al.*, 2016; Das *et al.*, 2018). No data is available on Pb isotopic signatures in context of the OWB source characteristic. However, some data are available for the waste incineration (burning of waste in incinerators), and related sources such as incinerator ash and residues (Monna *et al.*, 1997; Carignan *et al.*, 2005; Geagea *et al.*, 2008). These data may be useful, but the actual representation varies due to the differences in the compositions of waste and burning conditions.

Here we made an attempt to characterize metals emitted from the OWB practices and to understand their influence on urban aerosols, especially wintertime aerosols which are more likely to be influenced by OWB practices due to their increased frequency and magnitude. The objective of this study is to evaluate the influence of OWB emissions in urban aerosols using metal composition and Pb isotopic signature as a tool. We determined selected metals and Cr(VI) concentrations in OWB and urban aerosols. For the first time, here we report Pb isotopic composition of the OWB aerosols.

MATERIALS AND METHODS

Site Description

OWB sampling was performed at Okhla landfill, New Delhi as shown in Fig. 1. This is one of the active landfills with proper solid waste management practices. However, small fires keep breaking now and then. Hence this site was particularly chosen, as OWB can be observed here frequently. Moreover, for continuous sampling, we required a place where OWB could be observed for longer period. Similar sampling strategy was followed by Christian *et al.* (2010). Further details about the landfill and its waste composition have been given in Kumar *et al.* (2015). Briefly, Delhi's MSW (municipal solid waste) landfills consist of $55 \pm 20\%$ compostable materials with rest of the fraction as non-compostable material. Out of the non-compostable materials, recyclable materials (mainly polythene/plastic materials, foam, packing and packaging materials, metals, etc.) contribute to 20–30%, while rest are inert materials like construction and demolition waste, excavated soil, silt, etc.

Urban aerosol sampling was performed on the rooftop of National Physical Laboratory (NPL) building (~15 meters above the ground level [agl]). NPL site is located in central Delhi, which is about half a km away from the busy road, and is surrounded by institutional and residential areas, and protected-ridge vegetation. This makes it a well-mixed urban representative site. Another urban sampling site was a government building, i.e., Employees' State Insurance (ESI) hospital rooftop (~15 m agl). This building is situated at the foothills (Okhla landfill height is ~40 m agl) with nearby small shops, a bus depot and apartments with a sided busy road.



Fig. 1. Image of the sampling sites in Delhi, India (Google Earth imagery), and top-view photograph of ESI site.

Aerosol Sampling

OWB aerosol sampling was performed at Okhla landfill site on quartz filters (prebaked at 450°C, at least for 6 hours) using a high-volume air sampler (HVS, Vayubodhan Upkaran Pvt. Ltd.), which was operated at a flow rate of ~1100 litre per minute ($L \text{ min}^{-1}$). The sampler was placed on the downwind side of burning locations. Size segregated aerosol sampling was also performed to study the distribution of aerosol mass concentration in different size bins. Andersen sampler with eight stages and a backup stage having cutoff sizes of > 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65, 0.43 μm aerodynamic diameters was used. It operated at a flow rate of 28.3 $L \text{ min}^{-1}$. Aerosol samplings including high-volume (sample identity: HVS-102 to HVS-106, $n = 5$) and Andersen sampling were carried out for 2–3 hours during the daytime in October 2014. Since these are source samples, small sampling time is sufficient to capture the qualitative essence of characteristic OWB emissions.

Urban aerosol sampling was performed at NPL (during winter- and springtime) and ESI (during wintertime) sites. ESI site aerosol sampling was performed using HVS on 24 hourly basis starting at noon during 5–10 December 2011 (sample identity: HVS-230 to HVS-236, $n = 7$). Aerosol sampling at NPL site was done on 12 hourly basis using HVS, daytime sampling starting from ~7:00 to 19:00 and nighttime sampling from ~19:00 to 7:00. Springtime sampling was conducted during 22–24 March 2012 and 2–4 April 2012 (sample identity: HVS-230 to HVS-236, $n = 7$), whereas, wintertime sampling was performed on 28–31 December 2011 (sample identity: HVS-150 to HVS-158,

$n = 9$). It should be noted that daytime and nighttime variations of metals/metalloids in New Delhi aerosols are not very large (Kumar *et al.*, 2015), hence 12 and 24 hourly samplings are likely to present the similar results.

Size segregated aerosol samplings using Andersen sampler at NPL site were performed for running the sampler for 72 hours continuously. Wintertime samplings were started on 21 December and 26 December 2011, whereas springtime samplings on 3 April and 28 April 2012, respectively. Andersen sampling at ESI site was also carried out with a run time of 72 hours starting on 5 December 2011. Here it is important to note that urban aerosol samplings were done in 2011 and 2012, whereas landfill sampling was performed in 2014. Landfill samples were collected to see the metal and isotopic signatures of OWB aerosols, and then to infer their influence on the New Delhi aerosols, where OWB was observed to be a common practice (Gargava *et al.*, 2014) also in 2011–2012.

All filter samples were conditioned before and after sampling in a desiccator for gravimetric mass determination, and packed in a glass bottle. Samples were stored in a refrigerator until analysis.

Metal Analysis

For the determination of metals, filter samples were acid digested using a microwave digestion system (Multiwave Go-Anton Paar). A piece of filter (1.8 cm diameter punch cut) was taken in cleaned Teflon digestion vessel, then 7 mL HNO_3 (J.T. Baker ULTREX®) and 2 mL H_2O_2 (J.T. Baker ULTREX®) were added, and digested following the

procedure discussed in Kumar *et al.* (2015). Digested samples were transferred into the processed plastic bottles. Solution was finally filtered, weighed and diluted gravimetrically as per the requirement of the instrumental analysis. The samples were analysed for some specific metals (Cd, Cr, Cu, Fe, Ni, Pb, Se, Sn, Sr, V and Zn) and metalloids (As and Sb) using inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, NexION™ 300X). However, we have used collective term metals throughout the text for all metals and metalloids analysed in this study. NIST SRM 1648a (urban dust) was also analysed using the same procedure to check the recoveries of metals in the digestion process of aerosol samples. Recoveries lie in between 90 and 105% except for Sb and Sr (87–90%). Se and Sn are not certified in NIST SRM 1648a, hence their recoveries were not calculated. Concentrations of analysed metals in field blank samples were less than 5% of the minimum metal concentrations detected in the samples and less than 3% of the average concentration of metals determined in the samples. Also the variation in concentration of metals on repeatability (based on duplicate runs) of the samples is less than 3%. All the metal concentrations reported in the study are blank corrected.

Chromium(VI) Speciation

Sampling of aerosols for the analysis of Cr(VI) requires consideration of filter materials. Cellulose and glass fibre filters containing binders are unsuitable, as these filter types can lead to significant reduction of Cr(VI). However, polyvinyl chloride, polyvinyl fluoride, polytetrafluoroethylene (PTFE), PVC- and PVF-acrylic copolymers, and quartz fiber filters have been reported to be suitable for Cr(VI) analysis (Ashley *et al.*, 2003; Unceta *et al.*, 2010; Swietlik *et al.*, 2011). Further, determination of Cr(VI) content in aerosol samples involves four steps: extraction, separation, detection, and quantification. The extraction step for Cr(VI) is very important which decides whether soluble or total Cr(VI) is extracted. In acidic extraction methods, Cr(VI) is reduced to Cr(III). For the determination of water-soluble and sparingly soluble Cr(VI) in air filter samples, it is ordinarily recommended to use a buffer system of $(\text{NH}_4)_2\text{SO}_4$ – NH_4OH for extraction purposes as used in present study (Ashley *et al.*, 2003; Unceta *et al.*, 2010). In this study, a piece of aerosol filter sample was taken in a cleaned glass bottle, and 10 ml of $(\text{NH}_4)_2\text{SO}_4$ – NH_4OH buffer (0.5 M) at pH 8 was added to it, and was further ultra-sonicated for 90 minutes to dissolve soluble and sparingly soluble Cr(VI) in solution (further in text wherever we use Cr(VI) it means soluble Cr(VI)). Chromium speciation was carried out in the filtrate using a cation exchange stationary phase (column: DionexIonPac® CS5A [250 × 2.0 mm, 5 μm]) in conjunction with 100% acidic (0.85 M HNO_3) mobile phase. The HPLC-ICP-MS methodology was validated using a CRM (Inorganic Ventures CGCR[6]1-1). Analysis of Cr(VI) was done following the protocol discussed in McSheehy *et al.* (2008). Method detection limit (MDL) was determined using 3 times the standard deviation derived from the repeated measurements of calibration blank ($n = 5$), and found to be 0.03 ng m^{-3} .

All the results presented here are blank corrected.

Lead Isotope Analysis

Samples were also analysed for Pb isotopic ratios. From the extracts (digested extracts for metal analysis), further Pb was extracted using an ion exchange resin (Dowex® 1 × 8 100–200 mesh, Acros Organics) as discussed in the method given in Ortega *et al.* (2012) for isotope analysis. Briefly, acid was evaporated from the digested extracts, the residue was dissolved in dilute HBr and loaded on the column containing the resin for Pb extraction. Lead was extracted from the column using HCl, which was evaporated and the residue was re-dissolved in HNO_3 for isotope analysis. Isotope analysis was done using multi collector-ICP-MS (Nu Plasma, Nu Instruments, UK). Thallium (NIST 997, $^{205}\text{Tl}/^{203}\text{Tl} = 2.3871$) was added to the samples and standards to correct for instrumental mass bias using an exponential law. In addition, a sample standard bracketing correction using NIST 981 was applied as described in Ortega *et al.* (2012). Maximum Pb concentrations in filter blanks (i.e., the quartz filters used for sampling and used for Pb isotopic analyses) were less than 0.5% of Pb content in aerosol samples. Lead isotopic composition of NIST SRM 981 and NIST SRM 1648a (urban dust) measured in this study are shown in Table 1.

RESULTS AND DISCUSSION

Aerosol Mass Concentration and Size Distribution

Open waste burning emissions are associated with very high particulate emissions. This study found an average aerosol mass loading of $3780 \pm 2453 \mu\text{g m}^{-3}$ (range 1296–8242 $\mu\text{g m}^{-3}$) from the OWB emissions close to the source. This observation is consistent with the previous results ($n = 25$) which included sampling using handy samplers close to the OWB sources, i.e., $5855 \pm 3879 \mu\text{g m}^{-3}$ (range 1333–15833 $\mu\text{g m}^{-3}$) (Kumar *et al.*, 2015). According to an estimate, $\sim 145 \times 10^6$ tons of waste is generated per year in India and out of which 56% of total waste generated is burned (Wiedinmyer *et al.*, 2014). Wiedinmyer *et al.* (2014) estimated PM_{10} emission from OWB for 2010 to be 969×10^3 tons year^{-1} in India. This is $\sim 8\%$ of the total anthropogenic PM_{10} as estimated by EDGARv4.2 (Emission Database for Global Atmospheric Research), i.e., 11866×10^3 tons year^{-1} (note: this inventory does not include OWB as aerosol source). Further Wiedinmyer *et al.* (2014) reported that the contribution of OWB emissions in China is $\sim 22\%$ to the total anthropogenic PM_{10} as estimated by EDGARv4.2. These results suggest that total emissions are underestimated when OWB is not included in the source inventory.

In this study, it is difficult to generalize the findings and calculate the emission factor for OWB as (i) OWB conditions are not similar for every sampling performed, which might be impacted by the difference in the nature of waste, moisture, ambient temperature and supply of oxygen, etc., and (ii) also the composition of waste is non-homogeneous, which further limits the generalization. A lab simulation study reported that the largest PM emissions were observed from plastic combustion followed by other

Table 1. Lead isotopic composition determined in aerosol samples and standards in this study.

Sampling details	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
OWB aerosols							
2014 Oct 14	37.6437	15.5890	17.6618	2.1313	0.8826	1.1330	2.4148
2014 Oct 14	37.6413	15.5955	17.6909	2.1278	0.8816	1.1343	2.4136
2014 Oct 14	37.4978	15.5866	17.5755	2.1335	0.8868	1.1276	2.4058
Urban aerosols							
NPL springtime aerosols							
2012 Mar 23 Night	37.4302	15.5840	17.5019	2.1386	0.8904	1.1230	2.4018
2012 Apr 02 Night	37.4324	15.5827	17.5123	2.1374	0.8898	1.1238	2.4022
2012 Apr 03 Day	37.4731	15.5843	17.5641	2.1334	0.8873	1.1270	2.4045
2012 Apr 03 Night	37.4398	15.5862	17.5041	2.1389	0.8904	1.1230	2.4021
2012 Apr 04 Day	37.4569	15.5836	17.5298	2.1368	0.8890	1.1249	2.4036
NPL wintertime aerosols							
2011 Dec 19 Night	37.4645	15.5868	17.5396	2.1360	0.8887	1.1253	2.4036
2011 Dec 29 Day	37.4063	15.5844	17.4880	2.1389	0.8911	1.1221	2.4002
2011 Dec 29 Night	37.3950	15.5826	17.4723	2.1402	0.8918	1.1212	2.3998
2011 Dec 30 Day	37.3846	15.5804	17.4688	2.1400	0.8919	1.1212	2.3995
2011 Dec 28 Night	37.3785	15.5803	17.4685	2.1398	0.8919	1.1212	2.3991
2011 Dec 31 Day	37.4210	15.5816	17.4992	2.1384	0.8904	1.1230	2.4016
ESI wintertime aerosols							
2011 Dec 05 (24 h)	37.4781	15.5841	17.5639	2.1339	0.8872	1.1271	2.4049
2011 Dec 06 (24 h)	37.5367	15.5944	17.6009	2.1326	0.8860	1.1287	2.4071
2011 Dec 07 (24 h)	37.4458	15.5836	17.5438	2.1344	0.8883	1.1257	2.4029
2011 Dec 08 (24 h)	37.4962	15.5916	17.5702	2.1341	0.8874	1.1269	2.4049
Filter blank	37.4588	15.3475	17.8563	2.0962	0.8590	1.1641	2.4407
NIST SRM 1648a	38.8713	15.7154	19.4788	1.9956	0.8068	1.2394	2.4735
NIST SRM 981	36.7215	15.4915	16.9373	2.1681	0.9146	1.0933	2.3704

municipal solid waste (MSW, a combination of several combustibles and non-combustibles) combustion, paper combustion and wood combustion (Park *et al.*, 2013). This further suggests that plastic burning in wastes is a major concern as it adds to high PM emissions.

Mass concentration of urban aerosols is $732 \pm 157 \mu\text{g m}^{-3}$ ($n = 6$, range $508\text{--}979 \mu\text{g m}^{-3}$) and $590 \pm 157 \mu\text{g m}^{-3}$ ($n = 8$, range $405\text{--}863 \mu\text{g m}^{-3}$) at NPL in wintertime and springtime samples, respectively, whereas in ESI wintertime samples, it is $645 \pm 113 \mu\text{g m}^{-3}$ ($n = 4$, range $552\text{--}810 \mu\text{g m}^{-3}$). These mass loadings are higher than the average TSP concentrations compared to the previous study ($440 \pm 95 \mu\text{g m}^{-3}$) from the same NPL site conducted in winter 2006–2007 (Li *et al.*, 2014). However, the mean TSP concentration from New Delhi urban sampling site for the period September 2003 to August 2004 have been reported to be $546 \pm 176 \mu\text{g m}^{-3}$ (Shridhar *et al.* 2010), which is similar to the values (range $405\text{--}978 \mu\text{g m}^{-3}$) observed in this study.

Mass-size distribution of OWB and urban aerosols is shown in Fig. 2. High mass concentrations ($456 \pm 146 \mu\text{g m}^{-3}$) of OWB aerosols on ultra-fine mode (diameter $< 0.4 \mu\text{m}$) particles were observed compared to that of urban aerosols ($6\text{--}32 \mu\text{g m}^{-3}$). Mass concentration of $\text{PM}_{2.1}$ (summing up the mass concentrations from backup stage to $2.1 \mu\text{m}$ stages) is found to be ranged between 1625 and $2150 \mu\text{g m}^{-3}$ in OWB aerosols, whereas in urban $\text{PM}_{2.1}$, it is $124\text{--}177 \mu\text{g m}^{-3}$. Open waste burning $\text{PM}_{2.1}$ mass concentration values are at least 10-fold higher than that of

urban $\text{PM}_{2.1}$.

Further, Fig. 2 suggests that in urban wintertime aerosols, fine particle mass is peaked at size range $0.7\text{--}2.1 \mu\text{m}$, whereas upper mode peak appeared in the larger size range, i.e., $> 9.0 \mu\text{m}$. However, in spring season, fine mode is not distinct and overlapping with the coarse sized particles suggesting a continuous particle growth in springtime. In OWB aerosols, a peak appears in backup size ($< 4 \mu\text{m}$) range and another peak in $3.3\text{--}4.7 \mu\text{m}$ size. Fine mode peak is because of burning emission particles, whereas the coarse mode particle may be because of resuspension of upper soil dust being heated during burning activities. High mass concentration of OWB aerosols, as shown in the distribution suggests that these emissions are likely to contribute to fine aerosols significantly. Park *et al.* (2013) reported the results from the lab simulation of waste burning and concluded that $\text{PM}_{2.5}$ fraction exceeds 60% of the total suspended particulate matter.

Characteristics of OWB and Urban Aerosols

Winters in New Delhi, generally encounter a poor air quality which is accounted by increased anthropogenic emission of gases and particles from various combustion sources, decreased planetary boundary layer and poor ventilation because of geographical location of Delhi in Indo-Gangetic Plain (Shridhar *et al.*, 2010; Li *et al.*, 2014; Kumar *et al.*, 2016). Hence, the identification of these combustion sources and the chemical characterization of their emissions become important to better understand

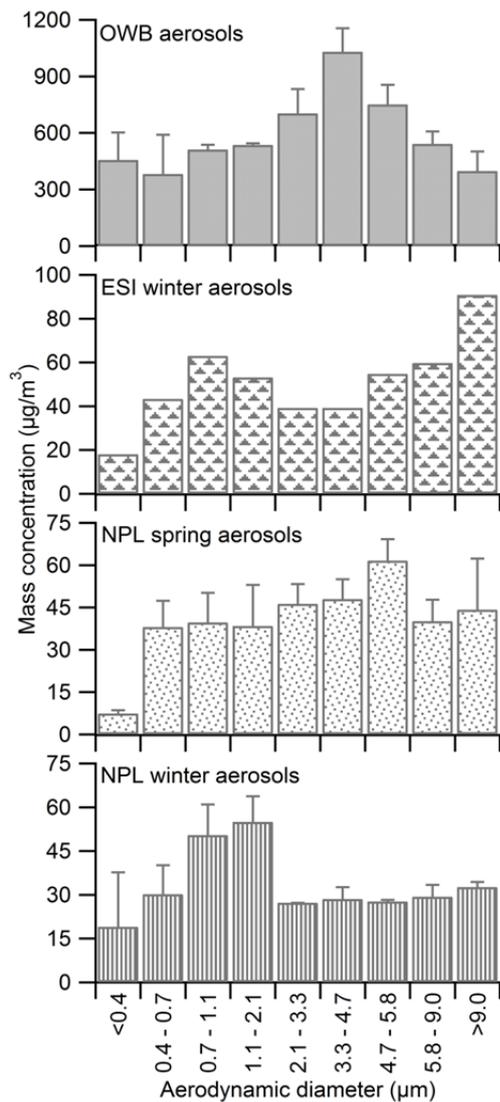


Fig. 2. Mass-size distribution of the OWB and urban aerosols.

these sources. One such urban source which is highly ignored, is the open burning of wastes. Open waste burning becomes more prominent during winters (Kumar *et al.*, 2015; Nagpure *et al.*, 2016). It is a common practice to burn wood for the purpose of warming up the ambience. However, in the urban areas of the developing countries where wood/biomass is not available to low-income group people, other alternatives like paper, plastics, tyres, and other combustibles in wastes are burnt as an energy source (Kumar *et al.*, 2015; Nagpure *et al.*, 2016).

Combustion processes are known to emit smoke and particles. Apart from the organics, metals are also released on combustion of wastes. Urban waste is enriched in paper, plastics, e-wastes and other combustibles. Kumar *et al.* (2015) have reported that organic matter, ions and metals comprised 75%, 8% and 0.8% in OWB and 31%, 31% and 1.6% in urban aerosols, respectively. This shows that the organics are the major components of the OWB emissions. However, there are few reports on the metal

emission characteristics of the OWB aerosols.

Further, an estimate suggested that municipal waste burned in Delhi ranged from 190 to 246 tons day⁻¹, about 2–3% of total generated MSW (Nagpure *et al.*, 2015). They further estimated that on an average daily municipal waste burned in Delhi in winter season ranged 236–263 kg km⁻² (38–40 incidents) and in summer season 206–246 kg km⁻² (25–31 incidents). This suggests that OWB becomes more prominent in winters. Also the composition of the waste burned in winters is more enriched in plastics compared to compostable wastes in summers (Nagpure *et al.*, 2015). Nagpure *et al.* (2015) found that in Agra, another city of India, OWB is more severe; ~24% (223 tons day⁻¹) of total waste produced is subjected to burning practices. This suggests that socio-economic status, awareness and regulations play an important role leading to OWB practices. Further, another report (NEERI [2010] based on factor analysis and CMB-8.2 applied to PM₁₀ using carbon, metals and ions data) suggests that OWB affects several sites in Delhi. Moreover, OWB has been found to have maximum contribution to aerosols in winter season can be as high as 52% as reported for one of the sampling sites in Delhi. In the same report at a background station (Prahadpur), OWB's contribution was found to vary 16–33% in between the seasons. These results strongly suggest that OWB is a major contributor to urban aerosols in Delhi and influence the characteristics of aerosols.

Globally, there are several reports suggesting the emission of metals from plastics, e-waste combustion and related recycling processes, and also from biomass burning (Gullett *et al.*, 2007; Wäger *et al.*, 2011). Plastics, e-wastes and biomass are the prominent components of urban wastes. Park *et al.* (2013) have estimated the emission factor of heavy metals, e.g., Pb, Ni, Cu, Cd, Cr and Zn, from the combustion of different materials in the wastes like paper, plastic, wood and mixed wastes, and found that the highest emission of total heavy metals was found in plastic followed by mixed wastes, paper and wood. This suggests that as the composition of plastic increases in mixed wastes, metal emissions will increase. New Delhi OWB aerosols have been reported to be containing high concentrations of As, Cd, Sb and Sn (Kumar *et al.*, 2015). Mixed plastic waste from electrical and electronic equipment has been also shown to be a significant contributor of heavy metals (As, Cd, Cr, Hg, Pb, Sb, Sn, etc.) (Gullett *et al.*, 2007; Wäger *et al.*, 2011).

In this study, we have characterized specific metals (As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) in OWB and urban aerosol samples. Their concentrations are summarised in Table 2. Metals which show explicitly high concentrations are Fe and Zn in all the samples (OWB + urban). Iron is often considered to be mostly coming from the crustal sources. Iron concentration in the aerosol samples analysed in this study varies in the range 8.36–46.70 µg m⁻³ (both these extreme values are found in OWB aerosols which is also reflected by large standard deviations) with an average 22.5 ± 9.26 µg m⁻³. Elevated average concentration of Fe (25.3 ± 8.57 µg m⁻³) in NPL springtime aerosols suggests that these aerosols are more

Table 2. Characteristics (mass and metal concentrations) of the OWB and urban aerosols.

$\mu\text{g m}^{-3}$	NPL Spring (Mar–Apr 2012)	NPL Winter (Dec 2011)	Okhla (Oct 2014)	ESI hospital (Dec 2011)
TSP	590 ± 157	732 ± 157	3781 ± 2454	645 ± 113
As	0.014 ± 0.002	0.029 ± 0.014	0.022 ± 0.006	0.022 ± 0.008
Cd	0.010 ± 0.005	0.039 ± 0.028	0.012 ± 0.008	0.010 ± 0.005
Cr	0.163 ± 0.041	0.267 ± 0.066	0.262 ± 0.177	0.137 ± 0.055
Cu	0.169 ± 0.070	0.494 ± 0.197	0.358 ± 0.231	0.113 ± 0.057
Fe	25.3 ± 8.57	18.3 ± 4.79	21.4 ± 13.6	24.5 ± 7.78
Ni	0.044 ± 0.013	0.063 ± 0.029	0.402 ± 0.291	0.059 ± 0.025
Pb	0.785 ± 0.403	3.593 ± 2.260	0.373 ± 0.165	0.499 ± 0.246
Sb	0.031 ± 0.032	0.116 ± 0.047	0.096 ± 0.051	0.021 ± 0.016
Se	0.005 ± 0.003	0.013 ± 0.004	0.005 ± 0.002	0.007 ± 0.001
Sn	0.041 ± 0.019	0.148 ± 0.082	0.211 ± 0.227	0.027 ± 0.017
Sr	0.176 ± 0.065	0.113 ± 0.047	0.290 ± 0.368	0.224 ± 0.070
V	0.060 ± 0.017	0.076 ± 0.071	0.067 ± 0.036	0.103 ± 0.039
Zn	0.941 ± 0.383	2.48 ± 0.863	1.60 ± 0.589	1.14 ± 0.444

influenced by crustal resuspension, whereas wintertime samples show comparatively lower concentration ($18.3 \pm 4.79 \mu\text{g m}^{-3}$), representing the lower contribution of crustal resuspension. However, Fe concentration is considerably higher than the previously reported $8.5 \pm 1.6 \mu\text{g m}^{-3}$ for TSP samples collected from the same NPL sampling site in winter 2006 and 2007 (Li *et al.*, 2014), but comparable with that of another New Delhi urban sampling site annual mean (September 2003 to August 2004), $16.4 \pm 4.65 \mu\text{g m}^{-3}$ (Shridhar *et al.*, 2010). It is observed that ESI wintertime aerosols have higher concentration of Fe ($24.5 \pm 7.78 \mu\text{g m}^{-3}$) which is comparable with NPL springtime samples ($25.3 \pm 8.57 \mu\text{g m}^{-3}$). The percentage contribution of Fe to TSP mass observed to be $\sim 2.5\%$ in NPL wintertime and $\sim 4.3\%$ in NPL springtime samples whereas it is $\sim 3.7\%$ in ESI wintertime, and $\sim 0.80\%$ in OWB samples. A comparative Fe concentration in urban springtime and ESI wintertime samples is probably because of the location of the ESI sampling site which is nearby a sided busy road leading to the resuspension of road dust.

Zinc concentration ($2.49 \pm 0.863 \mu\text{g m}^{-3}$) peaks in NPL wintertime aerosols as compared to other urban samples (0.941 ± 0.383 and $1.14 \pm 0.444 \mu\text{g m}^{-3}$ in NPL springtime and ESI wintertime aerosols, respectively). On the other hand, it is $1.60 \pm 0.589 \mu\text{g m}^{-3}$ in OWB aerosols. These concentration values are comparable with the previously reported values from the same sampling site in the winter season, i.e., $2.1 \pm 1.3 \mu\text{g m}^{-3}$ (Li *et al.*, 2014) and lower than the annual mean reported ($4.67 \pm 3.30 \mu\text{g m}^{-3}$) from another New Delhi urban site influenced by the industrial emissions for the period September 2003 to August 2004 and is comparable with the rural sampling site reported mean ($1.85 \pm 2.30 \mu\text{g m}^{-3}$) for the same period (Shridhar *et al.*, 2010). This suggests that Zn is locally enriched significantly from the anthropogenic sources. Zinc is related with several anthropogenic sources, e.g., Zn, Cu and Sb have been reported from traffic emissions (involves brake wear, combustion engine emissions, engine oil and road dust resuspension) (Bukowiecki *et al.*, 2009; Matawle *et al.*, 2009; Pant *et al.*, 2017). Zinc is also reported to be emitted from the smelting and heavy metal industries. Waste burning,

refuse incineration have been also reported to emit Zn, Cu and Pb (Christian *et al.*, 2010; Font *et al.*, 2015). This probably explains the high concentration of Zn in urban and OWB aerosol samples, and suggests the influence of OWB activities which might be negligible in size but their signatures at non-source locations are strong.

Further, metals which show intermediate concentration range are Cu, Cr, Ni, Pb, Sb, Sn, Sr and V. Order of mean concentration of these metals in OWB aerosols is $\text{Ni} > \text{Pb} > \text{Cu} > \text{Sr} > \text{Cr} > \text{Sn} > \text{Sb} > \text{V}$. In NPL wintertime aerosols, the order is $\text{Pb} > \text{Cu} > \text{Cr} > \text{Sn} > \text{Sb} > \text{Sr} > \text{V} > \text{Ni}$ compared to NPL springtime $\text{Pb} > \text{Sr} > \text{Cu} > \text{Cr} > \text{Sn} > \text{Sb} > \text{V} > \text{Ni}$ and in ESI wintertime aerosols it is $\text{Pb} > \text{Sr} > \text{Cr} > \text{Cu} > \text{V} > \text{Ni} > \text{Sn} > \text{Sb}$. Shridhar *et al.* (2010) have also reported the mean metal concentrations order $\text{Fe} > \text{Zn} > \text{Cu} > \text{V} > \text{Pb} > \text{Cr} > \text{Ni} > \text{Cd}$ from New Delhi urban and rural sites. Interestingly they reported the same order of metal concentrations from both sites (urban and rural) unlike the observation made in this study. Strontium concentrations in NPL springtime and ESI wintertime aerosols are higher in the order possibly due to increased influence of crustal sources as it is evident by the Fe concentration. Chromium concentration is found to be enhanced in OWB and NPL wintertime aerosols. High concentration of Cr has been found in the waste incineration residue (Astrup *et al.*, 2005; Pacyna *et al.*, 2007; Font *et al.*, 2015), which might be one of the reasons for enhanced Cr concentration in urban wintertime aerosols collected at NPL site (a point to be discussed in the following section). We observed some similarities in concentration ranges of the metals in OWB and ESI aerosols. Exceptional observation is the high concentration of Ni ($0.402 \pm 0.291 \mu\text{g m}^{-3}$), which is ~ 6 – 8 fold higher at OWB site as compared to the other sites. Open waste burnings and waste incinerations residues have been reported as one of the anthropogenic sources of Ni (Astrup *et al.*, 2005; Pacyna *et al.*, 2007; Christian *et al.*, 2010; Font *et al.*, 2015). Park *et al.* (2013) have also found Ni and Cr content in laboratory simulation of municipal waste burning aerosols.

Arsenic, Cd and Se show trace concentrations and are found almost comparable in all aerosol sample types.

Combustion of different fuels in stationary sources like boilers, industries, thermal plant, etc. have been reported to contribute for more than half of the anthropogenic emissions of these metal, i.e., As, Cd, Cr and Ni in Europe in 2000 (Pacyna *et al.*, 2007). Coal combustion in large power plants have been reported to contribute 18% and 17% to the total As and Cd emissions from anthropogenic sources in Europe in the year 2000, and another 17% and 17% contribution came from coal combustion in industrial boilers and small residential units, respectively. In addition, oil combustion in industrial boilers and residential units contributed 15% and 26% to the total anthropogenic emissions of As and Cd, respectively (Pacyna *et al.*, 2007). Selenium has been attributed to be emitted from anthropogenic sources like coal combustion in power plants, gasoline exhaust, diesel exhaust, coal fly ash and also biomass burning, and from natural sources, e.g., biogenic and crustal sources (Ellis *et al.*, 1993; Santiago *et al.*, 2014). In this study, concentration of Se is found to be in the range 0.001–0.021 $\mu\text{g m}^{-3}$. Highest average concentration of Se is found in NPL wintertime aerosols. Strong correlations ($r^2 > 0.5$) of Se and As concentrations (NPL wintertime samples = 0.96, ESI wintertime = 0.64, NPL springtime = 0.52, OWB = 0.09) were observed suggesting the possible contributions of coal combustion, vehicular exhaust, and biomass combustion sources.

We observed that Sn—a marker for OWB aerosols—shows the highest concentration ($0.211 \pm 0.227 \mu\text{g m}^{-3}$) in OWB aerosols. Urban NPL wintertime aerosols also show high concentration of Sn ($0.148 \pm 0.082 \mu\text{g m}^{-3}$). This enhanced concentration of Sn in NPL wintertime aerosols is likely due to the increased OWB frequencies in and around the residential areas (Kumar *et al.*, 2015; Nagpure *et al.*, 2015) nearby NPL site. Increased concentration of OWB marker elements clearly suggests strong influence of OWB emissions.

Chromium (VI) In OWB and Urban Aerosols

In the atmosphere, Cr is primarily found in aerosols in two oxidation states (+3 and +6) which are quite stable. Sources of Cr include natural as well as anthropogenic ones. Coal combustion in power plants, industries, and

residential units have been estimated to contribute 39% of anthropogenic Cr in Europe in 2000 (Pacyna *et al.*, 2007). Local sources of Cr are vehicular emissions, coal combustion at homes, coal-fired municipal heating plants, paint and a number of metalworking plants (Astrup *et al.*, 2005; Unceta *et al.*, 2010; Font *et al.*, 2015). Chromium(VI) is classified by US environmental protection agency as a group-A inhalation carcinogen. Toxicity of a species depends on its solubility and bioavailability. Because of high toxicity of Cr(VI), speciation study of Cr in aerosols is important for its correct evaluation. However, such speciation studies are scarce in aerosol matrices (Unceta *et al.*, 2010; Swietlik *et al.*, 2011; Huang *et al.*, 2014).

In this study, we determined total Cr using ICP-MS from acid digested samples. We observe significant concentration of Cr in aerosol samples as shown in Fig. 3. Hence, we determined the soluble Cr(VI) concentrations, i.e., Cr extractable using $(\text{NH}_4)_2\text{SO}_4\text{--NH}_4\text{OH}$ buffer (pH = 8) in these samples. As compared to urban aerosols, we observed a high concentration of Cr(VI) in the OWB aerosols. Chromium(VI) concentration in OWB aerosols is determined to be $7.3 \pm 1.4 \text{ ng m}^{-3}$ which exceeds the average urban concentration, i.e., $0.54 \pm 0.26 \text{ ng m}^{-3}$ by ~13-fold. Astrup *et al.* (2005) have reported considerable amount of Cr in residues from eight different municipal solid waste incinerators covering all major flue gas cleaning technologies and suggests that Cr(VI) species may be also present in the residue leachates.

In urban aerosols, Cr(VI) concentration was found to be 0.51 ± 0.11 , 0.74 ± 0.24 and $0.18 \pm 0.09 \text{ ng m}^{-3}$ in NPL winter-, NPL spring- and ESI wintertime samples, respectively, whereas soluble Cr(VI) percentage to total Cr is generally less or around 1% in all the samples as shown in Fig. 3. Huang *et al.* (2014) reported total Cr(VI) concentration in PM_{10} from New Jersey in winter and summer seasons, i.e., 1.05–1.41 and 0.99–1.56 ng m^{-3} , whereas that of soluble Cr(VI) 0.03–0.19 and 0.12–0.37 ng m^{-3} , respectively. They also observed higher soluble Cr(VI) concentration in summer samples consistent with our results where we also observed high Cr(VI) in NPL springtime samples. Huang *et al.* (2014) anticipated that the formation of Cr(VI) via atmospheric oxidation chemistry

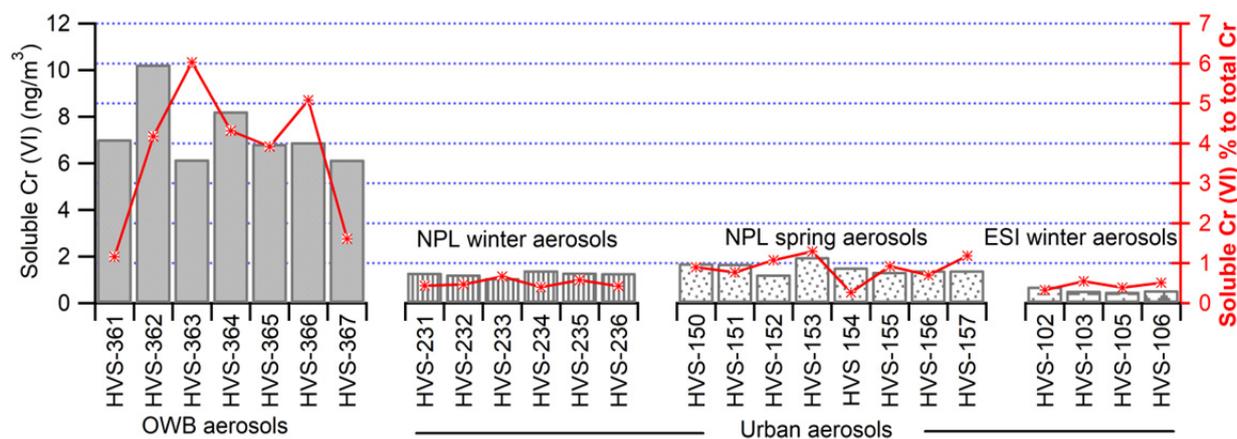


Fig. 3. Variation of Cr concentrations and percentage contribution of Cr(VI) to the total Cr in the OWB and urban aerosols.

may contribute to the higher soluble Cr(VI) concentrations in the summer.

Swietlik *et al.* (2011) found a mean concentration of 6.0 ng m^{-3} total Cr(VI) in TSP at Radom, Poland and found no particular local source for these species and attributed it to the industrial emissions. Our result suggests that OWB is an important source of soluble Cr(VI). Its contribution to total Cr is $\sim 1\text{--}6\%$ in OWB aerosols, while in urban samples this contribution is found to be less than or around 1%. Also the ratio of Cr to Sn (a tracer for waste burning aerosols) is similar in OWB and urban aerosols, i.e., ranged 0.66–4.8 and 0.76–7.5, respectively (it is important to note that apart from OWB aerosols, Cr has other anthropogenic sources as discussed above). Further, Sn shows a positive correlation ($r = 0.24$ and 0.17 in OWB and NPL wintertime aerosols, respectively) with Cr(VI). This suggests that OWB is an important source of Cr and soluble Cr(VI) in New Delhi urban aerosols. Apart from increased heavy metal concentrations, OWB emissions also have comparatively high concentration of toxic Cr(VI) species, marking an increased toxic influence.

Enrichment Factor Analysis

To get a better insight into the origin of elements in aerosols, soil etc., enrichment factors (EFs) are widely used. EF of a given element is calculated by finding the ratio of the concentration of that element in the sample normalized against the concentration of a conservative element (Al, Fe, Ti, etc.) to the concentration of the same element normalized to the conservative element in the earth's crust (Reimann and de Caritat, 2000). EFs can tell about its added concentration from the additional (e.g., anthropogenic) sources as compared to its background concentration. EF of a metal (X) is calculated as:

$$EF_X = \frac{\left(\frac{C_X}{C_{Ref}} \right)_{\text{Aerosol}}}{\left(\frac{C_X}{C_{Ref}} \right)_{\text{UCC}}} \quad (1)$$

where, C_X is the concentration of X , C_{Ref} is the concentration of a reference element in aerosol sample and upper continental crustal (UCC), respectively. For the calculation of EFs in aerosols, Fe can be taken as reference element as

has been taken in several studies. Concentration of metals in the earth's upper crust has been considered from the study as reported in Wedepohl (1995). EFs calculated in this study with UCC values from Wedepohl (1995) is shown in Fig. 4.

According to EFs, the element sources are classified into three groups, i.e., element with $EF < 10$ is considered to be a crustal origin without enrichment, $10 < EF < 100$ comes from mixed origins (crustal and anthropogenic sources), and $EF > 100$ indicates highly enriched and from anthropogenic sources (Shridhar *et al.*, 2010). Fig. 4, clearly shows that EFs of Cr, Ni (except for OWB aerosols), Sr, Ni and V are mostly < 10 , this represents that these metals are mainly originated from the crustal sources or soil resuspension. Further, it is important to note that Cr shows a slight enrichment in OWB and urban NPL wintertime samples suggesting possible influence of anthropogenic sources.

Further, Fig. 4 suggests that OWB samples are highly enriched in Cd, Sb and Sn and moderately enriched in Cu, Ni, Pb, Se and Zn. This suggests that Cd, Sb and Sn are significantly emitted from OWB, whereas Cu, Ni, Pb, Se and Zn possibly coming from OWB as well as soil resuspension. Urban winter- and springtime samples also show similar trends. Selenium shows moderate to high enrichment in all the samples. Higher enrichment of Se has been often associated with coal combustion but it has been also linked to vehicle exhaust and biomass burning sources (Ellis *et al.*, 1993; Santiago *et al.*, 2014). Cadmium, Cu, Pb, Sb, and Zn are comparatively more enriched in NPL wintertime. This further suggests that apart from the OWB there are other sources which contribute to these metals in the aerosols. Arsenic shows moderate enrichment, indicating its mixed sources. Interestingly, Ni which shows crustal sources for urban aerosols has a higher enrichment for OWB aerosols showing moderate enrichment. As discussed earlier, the composition of waste is not uniform and hence this might be one of the reasons for the high Ni content in the OWB aerosols.

Lead Isotopic Signatures in OWB Aerosols and a Comparison with Urban Aerosols

Lead is a widely used metal and its sources in the environment are production (mining and smelting processes), usages (lead-acid storage batteries, pigments, ammunition, cable sheathing, weights for lifting, weight belts for diving, lead crystal glass, radiation protection and in various alloys), disposal, recycling, leaching (solid waste, contaminated

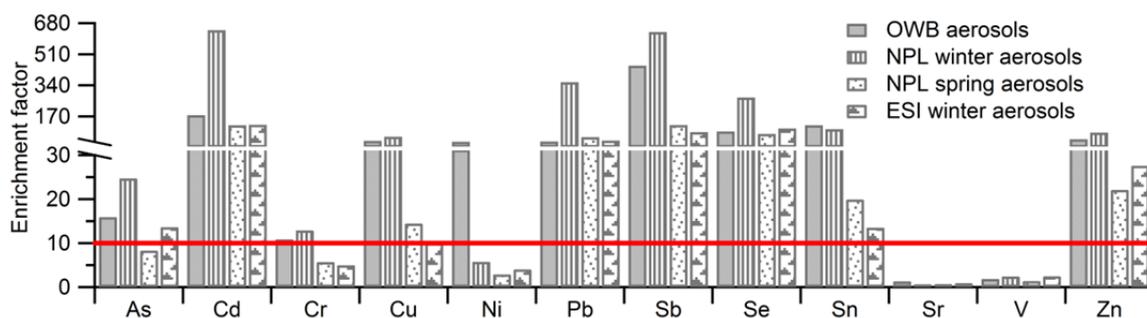


Fig. 4. Enrichment factor of the metals (with respect to Fe) in the OWB and urban aerosols.

sources and other open sources available), combustion of fossil fuels and other combustibles (coal, wood, petroleum products, tires, plastics, paints, etc.), use of mineral fertilizers and sewage sludge application, etc. (Zhao *et al.*, 2015).

Waste incinerations and OWB practices have been reported to release Pb in the atmosphere (Monna *et al.*, 1997; Carignan *et al.*, 2005; Geagea *et al.*, 2008; Komárek *et al.*, 2008; NEERI, 2010). Emission of Pb in Delhi has been estimated to be 203 kg day⁻¹ for the year 2007 (Gargava *et al.*, 2014). The permissible limit of Pb in particulate matter defined in the ambient air quality standards is 1 µg m⁻³ for 24 hour aerosol samples (Aggarwal *et al.*, 2013). In this study Pb concentration is found to be 3.59 ± 2.26 and 0.785 ± 0.403 µg m⁻³ in NPL winter- and springtime samples, respectively, whereas it is 0.499 ± 0.256 µg m⁻³ in ESI wintertime samples. Interestingly, Pb concentration in OWB samples was found to be the lowest, i.e., 0.373 ± 0.165 µg m⁻³. In previous studies from Delhi similar Pb concentrations (1.40 ± 0.94 µg m⁻³) in wintertime TSP samples (Li *et al.*, 2014), annual mean 0.41 ± 0.21 and 0.25 ± 0.25 µg m⁻³ in TSP urban and rural samples, respectively (Shridhar *et al.*, 2010), have been reported. It has been estimated that daily emission of Pb in Delhi due to OWB

practices (waste burning data in Delhi from Nagpure *et al.*, 2015) is ~3.06–3.90 kg of Pb (lower estimate) and ~15.29–19.51 kg of Pb (upper estimate) considering the emission factor of Pb 0.01–0.05 mg kg⁻¹ MSW (Park *et al.*, 2013). This estimate comprises 1.5–1.9% (lower) and 7.5–9.6% (upper) of total Pb emission estimated in 2007 (the annual estimate of 203 kg day⁻¹ (Gargava *et al.*, 2014). However as discussed above, Pb has several sources. Therefore, Pb isotopic study might be a helpful tool in providing a better insight for contribution of OWB in urban aerosols.

In spite of its robustness, this technique requires a wide array of Pb isotopic data from the region and contributing sources. According to the best of our knowledge no Pb isotope study has been done for the OWB aerosols. There are some studies on Pb isotopic ratios available for the waste incinerator emissions (Monna *et al.*, 1997; Carignan *et al.*, 2005; Geagea *et al.*, 2008; Komárek *et al.*, 2008).

We have analysed a limited number of samples of OWB aerosols and urban aerosol samples for their Pb isotopic compositions (Table 1). Fig. 5(a) shows the three isotope plot of ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁶Pb/²⁰⁷Pb for the OWB and urban aerosols. Pb isotopic signature of OWB aerosols, i.e., ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁷Pb ratios are 2.1309 ± 0.0029

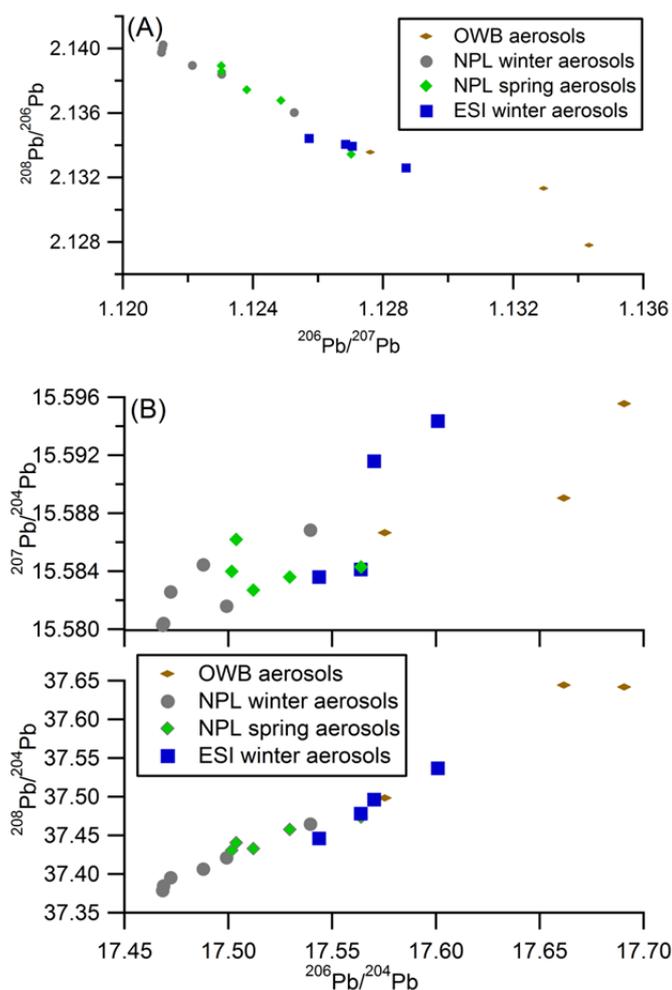


Fig. 5. Lead (Pb) three isotope plots of the OWB and urban aerosols, (a) ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁶Pb/²⁰⁷Pb and (b) ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb.

and 1.1316 ± 0.0035 and that of urban aerosols are 2.1369 ± 0.0026 and 1.1243 ± 0.0024 , respectively. All isotopic ratios lie along a straight mixing line, suggesting mixing of end member sources. On the other hand, $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ are plotted in Fig. 5(b) for OWB and urban aerosols. Fig. 5(b) upper panel shows scatter in the plotted values which suggest several anthropogenic sources contributing to Pb content in aerosols. However, the lower panel shows linear data points suggesting similarity in the anthropogenic mixing sources.

Natural sources of Indian Pb, e.g., ores, desert sand and rock, have been plotted in Fig. 6. It is interesting to note that the Pb isotopic signatures of galena from the Lesser Himalayas (Sarkar *et al.*, 2000) are less radiogenic compared to that galena which is found in Northwestern India (Deb *et al.*, 2001) (Fig. 6). Delhi has two major geographic features, the Yamuna floodplains fed by Yamuna River and the Delhi Ridge, an extension of Aravalli Range in Northwestern India. Hence the natural Pb isotopic ratio is likely to be influenced by both the diverse sources. Apart from this, Pb isotopic ratios for Mt. Everest rock/sand and the Thar Desert sand (Burn-Nunes *et al.*, 2014) has been also incorporated to get a natural mixing line of the Pb isotopic data from the Indian region (Fig. 6). Aerosol signatures from the region have been observed to be almost parallel to the natural line of $^{208}\text{Pb}/^{204}\text{Pb}$, suggesting the similar sources for ^{208}Pb to that of natural sources. However, the natural line of $^{207}\text{Pb}/^{204}\text{Pb}$ is not very close to

the aerosol signatures from the region, suggesting that the aerosols are affected by some other sources which have lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. Since there are not sufficient anthropogenic end-member data from the region, it is difficult to ascertain the anthropogenic sources affecting aerosols. A closer look at Fig. 6, inset figures with available data from literature suggests that the Pb isotopic compositions of the aerosols from this study are not specifically showing any particular source influence of the Kolkata diesel signature (Das *et al.*, 2018), and closely overlap with the Kolkata street dust signatures.

Further, a common observation is that Pb isotopic ratios in OWB are comparatively more radiogenic than that of urban aerosols. This suggests the influence of soil/dust which also gets resuspended during the burning of waste material on the ground surface, also evident by the more radiogenic signatures of the Kolkata street dust signatures (Das *et al.*, 2018). As observed in Fig. 5, it is difficult to distinguish the Pb isotopic signatures between OWB and urban aerosols. In both aerosol types these signatures are overlapped, suggesting a considerable influence of the OWB aerosols on urban New Delhi aerosols.

CONCLUSIONS

Aerosol samples were collected from an open-waste burning (OWB) site, viz., the Okhla landfill, in New Delhi. Also, urban samples were collected on the rooftops of the

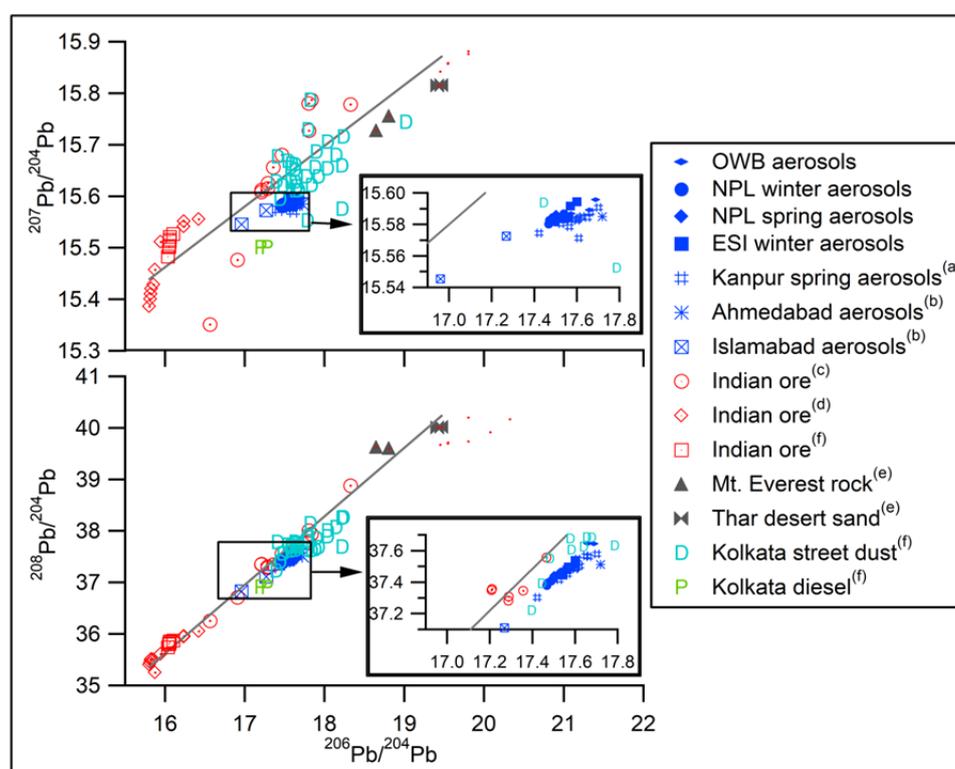


Fig. 6. Natural mixing line of Pb isotope from the Indian region based on Indian ores (^(c)Deb *et al.*, 2001; ^(d)Sarkar *et al.*, 2000; ^(f)Das *et al.*, 2018), Thar desert sand, Mt. Everest rock/sand and calculated natural background (^(e)Burn-Nunes *et al.*, 2014). Lead isotopic composition of aerosols from this study and previous studies (^(b)Bollhöfer and Rosman, 2001; ^(a)Sen *et al.*, 2016) and some source members (^(f)Das *et al.*, 2018) have been also plotted.

National Physical Laboratory (NPL) building (in winter and spring) and the Employees' State Insurance (ESI) hospital building (in winter), located in the foothills of the Okhla landfill and beside a busy road. High mass loading of OWB particles was observed, which was prominent in the fine mode. Aerosol samples were analysed for specific metals, and the metal concentrations in the OWB and NPL wintertime aerosols were found to be comparable. The concentrations of Sn and Sb, proposed tracers for emissions from open waste burning, were higher in the OWB aerosols (0.211 ± 0.227 and $0.096 \pm 0.051 \mu\text{g m}^{-3}$, respectively) than the urban ones (0.075 ± 0.071 and $0.060 \pm 0.054 \mu\text{g m}^{-3}$, respectively), which suggests that OWB contributes considerably to urban aerosols. The order of the metal concentrations in the OWB aerosols was $\text{Fe} > \text{Zn} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Sr} > \text{Cr} > \text{Sn} > \text{Sb} > \text{V} > \text{As} > \text{Cd} > \text{Se}$, exhibiting some similarity to that of the urban aerosols. However, the concentrations of some metals (Pb, Se and V) in the urban aerosols exceeded those in the OWB aerosols, suggesting the influence of other sources in the former. The concentration of soluble Cr(VI) and its contribution to the total Cr was found to be higher in the OWB aerosols ($7.3 \pm 1.4 \text{ ng m}^{-3}$, ~1–6%) than the urban aerosols ($0.54 \pm 0.28 \text{ ng m}^{-3}$, < 1%). However, the Cr to Sn ratios in the OWB and urban aerosols were similar, ranging 0.66–4.8 and 0.76–7.5, respectively, suggesting that OWB is one of the sources of Cr and Cr(VI) in urban aerosols.

Studying the enrichment factors (EFs) revealed that Sb and Sn were specifically enriched in the OWB aerosols, and similar results were found for the urban aerosols, especially in the NPL winter aerosols. The EF analysis also confirmed mixed sources for the Zn in the urban and OWB aerosols, suggesting that OWB is one of the likely sources. The very high enrichment of Se in all the aerosol types may indicate the influence of coal combustion, vehicle exhaust and biomass burning.

The lead isotopic ratios of these aerosols were measured, and the compositions of the OWB aerosols were reported, to the best of our knowledge, for the first time. Our results clearly show the influence of OWB on urban aerosols, as the Pb isotopic signatures of the OWB and urban aerosols overlap significantly. Furthermore, this study highlights the need to control OWB practices, as their contribution to the fine particulate matter may be excessively high and lead to adverse health effects. Although open waste burning is small in magnitude, the incidence is high compared to events from bigger combustion sources; thus, neglecting the pollution from OWB may result in the underestimation of emissions.

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