Atmospheric Environment 108 (2015) 49–58

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

# Investigation of the tracers for plastic-enriched waste burning aerosols

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## HIGHLIGHTS

- Chemical composition of plastic-enriched waste burning aerosols.
- Discusses organics versus metals for a better tracer of waste burning aerosols.
- Suggests that terephthalic acid is a good tracer for such fresh particles.
- Whereas phthalic acid is a tracer for aged particles influenced with waste burning.
- Suggests that tin is a better tracer for plastic-enriched waste burning aerosols.

## ARTICLE INFO

*Article history:*
Received 25 November 2014
Received in revised form
23 February 2015
Accepted 26 February 2015
Available online 26 February 2015

*Keywords:*
Plastic waste burning aerosol
Chemical composition
Tracer
Metals
Diacids
Phthalic acid formation pathway

## ABSTRACT

To better identify the tracers for open-waste burning (OWB) aerosols, we have conducted aerosol sampling at 2 landfill sites, i.e., Okhla and Bhalswa in New Delhi. The metals such as, As, Cd, Sb and Sn, which have been observed almost negligible in remote aerosols, are found abundantly in these OWB aerosol samples ($n = 26$), i.e., $60 \pm 65$, $41 \pm 53$, $537 \pm 847$ and $1325 \pm 1218$ ng $m^{-3}$, respectively. Samples ($n = 20$) collected at urban locations in New Delhi, i.e., at Employees' State Insurance (ESI) hospital and National Physical Laboratory (NPL) also show high abundances of these metals in the particles. Filter samples are also analyzed for water-soluble dicarboxylic acids ($C_2$–$C_{12}$) and related compounds (oxo-carboxylic acids and α-dicarbonyls). Terephthalic acid (tPh) was found to account for more than 77% of total diacids determined in OWB aerosols. However, such a high abundance of tPh is not observed in aerosols collected at urban sites. Instead, phthalic acid (Ph) was found as the third/fourth most abundant diacid (~3%) following $C_2$ (>70%) and $C_4$ (>12%) in these waste burning influenced urban aerosols. A possible secondary formation pathway of Ph by photo-degradation of phthalate ester (di-2-ethylhexyl phthalate) in plastic-waste burning aerosol is suggested. Ionic composition of OWB aerosols showed that $Cl^-$ is the most abundant ion ($40 \pm 8$% of total ions determined). The correlation studies of the potential metals with the organic tracers of garbage burning, i.e., phthalic, isophthalic and terephthalic acids show that especially Sn can be used as marker for tracing the plastic-enriched waste burning aerosols.



## 1. Introduction

Identification of aerosol sources is a priority for air quality strategy, aerosol health impact and climate change study. However, it is a difficult task as aerosols have several sources and involved in complex atmospheric processing, degradation and removal processes. Several approaches have been used for this task, e.g., models, which are based on the input of chemical species (Amato et al., 2011; Li et al., 2012; Pant and Harrison, 2012), stable- and radioisotope compositions of certain species (Aggarwal et al., 2013a; Aggarwal and Kawamura, 2008; Kirillova et al., 2014; Wang et al., 2012), chemical markers (Simoneit et al., 1999), in which trace metals are the better options because they persist in the atmosphere throughout the life of a particle.

Open-waste burning (OWB) practices are commonly reported in several parts on the globe including India, China, Mexico, Tanzania,

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http://dx.doi.org/10.1016/j.atmosenv.2015.02.066
1352-2310/

Mongolia, etc. (Christian et al., 2010; Fu et al., 2010; Jung et al., 2010; Kassim, 2006; Kawamura and Pavuluri, 2010; Li et al., 2012; Mkoma and Kawamura, 2013; Wang et al., 2012). OWB is accompanied with smoke rich emission, which comprises greenhouse gases, toxic gases and particle-bound chemicals (Wiedinmyer et al., 2014). Instead most garbage burning occurs in proximity close to residential areas or public places. In several megacities, garbage is generally burned to minimize the waste. The dumped municipal solid waste (MSW) at landfill sites is often burned (Christian et al., 2010; Kawamura and Pavuluri, 2010; Pavuluri et al., 2010). Garbage burning in the backyard by the locals is also common in several countries (Lemieux et al., 2000). In developing world, these practices are even more common, where waste is burned at street sites, nearby houses, apartments and local markets (Wiedinmyer et al., 2014).

Christian et al. (2010) estimated that about 2000 Tg year$^{-1}$ of garbage is generated globally and about the half is burned in open fire or incinerators. For an example, in Tanzania alone, dumping of MSW (containing large amounts of plastic) into open landfills is very common, and ~60% of daily domestic solid waste are disposed and subjected to open burning (Kassim, 2006). Therefore, garbage burning is one of the important sources of aerosols, which is largely overlooked (Wiedinmyer et al., 2014). In most of the reports such burnings are clubbed with biomass burning aerosols (Akagi et al., 2011), or fuel burning aerosols (Lei et al., 2013).

OWB has been reported to be a prominent source of particulate chloride in the urban and suburban areas (Christian et al., 2010). In Mexico City, the contribution of open-waste burning to $PM_{2.5}$ particulate chloride is more than 60% of the total measured chloride. An estimate suggests that HCl generated by these sources is as high as 6–9 Tg year$^{-1}$ globally. OWB in Mexico contributes to 3–30% of the $PM_{2.5}$ mass (Li et al., 2012). On the other hand, the emissions of $PM_{10}$ from OWB in China have been estimated to 22% of China's total reported anthropogenic $PM_{10}$ emissions (Wiedinmyer et al., 2014). Also in China, MSW landfills have been recognized to contribute to the increasing concentration of mercury in the ambient air. Annual estimate of mercury emissions from 5 landfills in China has been obtained to range from 17 to 3300 g year$^{-1}$ (Li et al., 2010).

These recent studies pointed out the requirement of better understanding the emissions from OWB and hence a need to perform more studies (on different parts of the world) to quantify the emissions. New Delhi the capital of India is situated within the metropolis of Delhi National Capital Territory (NCT) which is one of the largest metropolises by area (~1500 km$^2$) and the second largest by population (~17 million, 2011) in India (http://ncrpb.nic.in/). Several fold high aerosol mass loading is observed in New Delhi than that defined in National Ambient Air Quality Standards (NAAQS) (Aggarwal et al., 2013b), especially in winter season (Miyazaki et al., 2009). In New Delhi, open burning of garbage at road sides, residential campuses and local markets is a common practice. Sometimes it is just to dispose of the waste, but in the severe winter, it is one of the easily available refuges to get over cold for many people in the megacity. Common materials in these trashes are plastic bags, bottles and packing materials apart from paper waste, clothes, etc. Such waste material is mainly dumped at three working landfill sites in Delhi.

Our research objective is to find a better tracer for OWB aerosols. Unlike the organic tracers that tend to undergo physicochemical transformation during atmospheric transport from source to the receptor, we focus here on the metals that can be quantified without any ambiguity as long as particles remain suspended. For this purpose, we performed aerosol sampling at the source of OWB, nearby source at an urban site and a well-mixed urban representative site. The samples were analyzed using ICP-HRMS for specific metals, which could be used as potential source tracer. In addition, few samples were also analyzed for organic acids, which are known as organic tracer for waste burning aerosols. We study the relation of these organic tracers with the metal tracers. In this paper, we discuss the possibility of tin (Sn) as a source tracer for plastic-enriched waste burning aerosols.

## 2. Materials and methods

### 2.1. Site description and sampling details

Aerosol sampling was performed in New Delhi at the OWB sites (Okhla and Bhalswa landfills), nearby source at an urban site (rooftop of Employees' State Insurance (ESI) hospital building) and at a well-mixed urban representative source site (rooftop of NPL building) as shown in Fig. 1. The information about landfill sites has been given in Chakraborty et al. (2011). Waste composition at Delhi's MSW landfills consists of 55 ± 20% compostable material with rest of the fraction as non-compostable material. Out of the non-compostable materials, recyclable materials (mainly polythene/plastic materials, foam, paper, packing and packaging materials, clothes, etc.) contribute to 20–30%, while rest are inert materials like construction and demolition waste, excavated soil, silt, etc. (Chakraborty et al., 2011). Compostable material also consists of biomass (including garden waste), and food materials from kitchen waste. Based on the annual estimation, about 1200 and 1500 tons day$^{-1}$ of waste is dumped in Okhla and Bhalswa landfills, respectively. About 7500 tons year$^{-1}$ of $CH_4$ emission is estimated from Okhla landfill alone (Chakraborty et al., 2011).

Nearby Okhla landfill site, a government building, i.e., ESI hospital is situated at the foothills (Okhla landfill height is approximately 40 m above the ground level). This building is located nearby small shops and apartments with a sided busy road. NPL site is located in central Delhi, which is about half km away from the busy road, and is surrounded by institutional and residential areas, and protected ridge vegetation (Fig. 1). Sampling at NPL and ESI hospital sites was carried out on the rooftop (~15 m height above the ground level), on quartz filters (prebaked at 450 °C) using a high-volume air sampler (Vayubodhan Upkaran Pvt. Ltd.), which was operated at a flow rate of 1100 L per minute (lpm). Most of the samplings at the landfills were carried out using low-volume handy sampler (Envirotech Instruments Pvt. Ltd., APM 821), which was placed in downwind direction to fire break location. Handy sampler was placed at a height of ~2.5 m above the ground level (agl) and operated at a flow rate of 2 lpm. Samples were also collected using a high-volume air sampler at the landfill sites ~1 m agl, and~ 30 m away from the fire break location.

It is important to note that the chemical compositions determined in handy sampler samples (collected at ~2.5 m agl with 2 lpm flow rate) and high-volume samples (collected at ~1 m agl with 1100 lpm flow rate) were found to be similar. This comparison suggests that the chances of contamination of ground dust with smoke particles in high-volume samples were insignificant. Moreover for landfill sites, most of the samples considered in this study are low-volume handy sampler samples. Sampling details are summarized in Table 1. Total 38 samples and 8 field blank samples from different sites were considered in this study. 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.

### 2.2. Analyses

For the determination of metals, filter samples were acid digested using a microwave digestion system (Berghof MSW3+). A piece of filter was taken in cleaned Teflon digestion vessel and 5 ml