Atmospheric Environment 125 (2016) 505–511

Contents lists available at ScienceDirect

Atmospheric Environment

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

Risk assessment of bioaccessible trace elements in smoke haze aerosols versus urban aerosols using simulated lung fluids

Xian Huang, Raghu Betha, Li Yun Tan, Rajasekhar Balasubramanian*

Department of Civil and Environmental Engineering, National University of Singapore, Singapore

HIGHLIGHTS

- Bioaccessbility of particulate-bound trace elements using simulated lung fluids.
- Dissolution kinetics of 13 trace elements in simulated lung fluids.
- Evaluation of bioaccessibility of 13 elements in both haze and non-haze samples.
- Health Risk assessment for three possible scenarios upon inhalation of $PM_{2.5}$.
- Underestimation of health risk assessment while using water as a leaching agent.

ARTICLE INFO

Article history:
Received 9 March 2015
Received in revised form 17 June 2015
Accepted 19 June 2015
Available online 20 June 2015

Keywords:
Metal bioaccessibility
Simulated lung fluids
Smoke haze
Health risk assessment
Aerosols

ABSTRACT

Smoke-haze episodes, caused by uncontrolled peat and forest fires, occur almost every year in the South-East Asian region with increased concentrations of $PM_{2.5}$ (airborne particulate matter (PM) with diameter $\leq$ 2.5 μm). Particulate-bound trace elements (TrElems), especially carcinogenic and toxic elements, were measured during smoke haze as well as non-haze periods in 2014 as they are considered to be indicators of potential health effects. The bioaccessibilities of 13 TrElems were investigated using two types of simulated lung fluids (SLFs), Gamble's solution and artificial lysosomal fluid (ALF), instead of the commonly used leaching agent (water). The dissolution kinetics was also examined for these TrElems. Many TrElems showed higher solubility in SLFs, and were more soluble in ALF compared to the Gamble's solution. Cu, Mn and Cd were observed to be the most soluble trace elements in ALF, while in Gamble's solution the most soluble trace elements were Cu, Mn and Zn. The dissolution rates were highly variable among the elements. Health risk assessment was conducted based on the measured concentrations of TrElems and their corresponding toxicities for three possible scenarios involving interactions between carcinogenic and toxic TrElems and SLFs, using the United States Environmental Protection Agency (USEPA) human health risk assessment model. The cumulative cancer risks exceeded the acceptable level (1 in a million i.e. 1×10^{-6}). However, the estimation of health quotient (HQ) indicated no significant chronic toxic health effects. The risk assessment results revealed that the assessment of bioaccessibility of particulate-bound TrElems using water as the leaching agent may underestimate the health risk.

1. Introduction

PM has been a major concern globally due to its adverse environmental and health impacts. Many epidemiological studies have demonstrated the associations between high concentration of PM and increased mortality and morbidity of cardio-pulmonary diseases (Brunekreef and Holgate, 2002; Emmanuel, 2000; Pražnikar and Pražnikar, 2012; Russell and Brunekreef, 2009). These adverse health impacts of PM are particularly pronounced in urban areas due to the presence of intense anthropogenic emission sources and concentrated exposed population (Wiedensohler et al., 2002; Xinfu, 1999). Singapore being an urbanized country has several local anthropogenic PM emission sources including on-road vehicles and industries (Balasubramanian et al., 1999, 2003; Balasubramanian and Qian, 2004). In addition to

* Corresponding author. Department of Civil and Environmental Engineering, National University of Singapore, 117576, Singapore.
E-mail address: ceerbala@nus.edu.sg (R. Balasubramanian).

http://dx.doi.org/10.1016/j.atmosenv.2015.06.034
1352-2310/

these local sources, the air quality in Singapore is also affected sporadically by episodic trans-boundary regional "smoke-haze" episodes, caused by wild forest and peat fires due to land clearing activities in the neighbouring Indonesian provinces of Sumatra and Kalimantan (Balasubramanian et al., 1999, 2003; Betha et al., 2014; Orlic et al., 1999; Velasco and Roth, 2012). Smoke haze episodes lead to increased atmospheric particle loading and severe health impacts (Rappold et al., 2011). While the chemical composition and health effects of urban PM have been widely studied, the health impacts of smoke haze influenced PM remain incompletely understood. It is, therefore, important to study the significance of the health impacts of smoke haze in relation that of urban PM, so that appropriate remedial actions can be taken to improve urban air quality and mitigate its adverse health impacts.

Trace elements (TrElems) present in PM play a significant role in inducing health effects (Adamson et al., 2000). Many carcinogenic TrElems (e.g., cadmium, lead, and arsenic) have been detected in PM in many places (e.g., Boman et al., 2010; Lü et al., 2012). It is believed that the transition metals (e.g., nickel, iron, and copper) can produce reactive oxygen species (ROS) and cause inflammation to the human lung upon inhalation (Carter et al., 1997; Fuchs, 2001; Karthikeyan et al., 2006a, 2006b; Lu et al., 2011, 2015). The potential health effects of trace metals in PM depend on their total contents, their bioavailability, their relative toxicity and a number of factors related to inhalation exposure (Karthikeyan et al., 2006a, 2006b). Estimating the bioavailability of particulate-bound TrElems is an important step in assessing human health risks. The water-soluble fraction of trace metals is usually considered to represent their bioavailability (Karthikeyan et al., 2006a, 2006b; Manousakas et al., 2014). However, the chemical constituents of the lung fluids are different from those of ultrapure water, and the difference in the ionic strength of the dissolution media would have significant impacts on the solubility of the particulate metals and hence the related potential health risk (Davison et al., 1994). Julien et al. (2011) studied the solubility of TrElems in simulated lung fluids (SLFs) and in ultrapure water, and concluded that more metals were dissolved in SLFs. Hence, artificial body fluids are preferred to ultrapure water as the leaching agent for the bioaccessibility estimation studies (Davies and Feddah, 2003; Karthikeyan et al., 2006a, 2006b; Marques et al., 2011). Artificial body fluids have been used to assess the health risk of certain metallic compounds in many studies. Midander et al. (2007) have studied the leaching performance of copper (Cu) from different powder copper materials in four types of artificial fluids. Stopford et al. (2003) have measured the solubility of Cobalt (Co) compounds in six simulated body fluids (including SLFs) and serum. However, limited studies have used the SLFs to study the dissolution of TrElems in PM (da Silva et al., 2015). To the best of our knowledge, no study has been conducted to investigate the bioaccessibility of TrElems in haze aerosols in relation to urban aerosols using SLFs, despite its importance in the prediction of the uptake of TrElems by the human lung (Stopford et al., 2003).

The key objective of this study is to investigate the dissolution kinetics and bioaccessibility of trace element constituents present in $PM_{2.5}$ influenced by smoke haze plumes transported over a long distance as well as in the background urban $PM_{2.5}$. For this work, the Gamble's solution and the artificial lysosomal fluid (ALF) were employed as surrogate human lung fluids to simulate different conditions in the human lung pertaining to an inhalation scenario. The former solution with a pH 7.4 is analogous to the interstitial fluid deep inside the lung while the latter solution of pH 4.5 mimics the intracellular conditions in lungs occurring in conjunction with phagocytises. The associated risk assessment is also estimated using both SLFs and compared to that using water soluble fractions of total elements concentration.

2. Material and methods

2.1. PM sample collection

$PM_{2.5}$ samples were collected from January to September of 2014 (68 samples) with a mini-volume sampler, equipped with an impactor at the inlet to remove particles larger than $PM_{2.5}$ (with an airflow rate of 5 L per minute) at the atmospheric research station (latitudes 1° 18′ N and longitudes 103° 46′ E, 67 m above sea level) located at the roof top of one of the tallest buildings in the Engineering faculty, National University of Singapore. The collection time was 24 h for haze samples and 48 h for non-haze samples to ensure that sufficient mass of $PM_{2.5}$ was collected for chemical analysis. 47 mm quartz microfiber filters (Whatman, UK) were used for sample collection and pre-conditioned in a dry box maintained at 22 °C and 33% relative humidity for at least 24 h and weighed using a microbalance (Sartorius, MC 5) before sampling. Similarly, post-sampling conditioning and weighing were performed so that the gravimetric mass of the collected $PM_{2.5}$ can be obtained by deducting the initial filter weight from the filter weight after sampling. The PM samples were stored at 4 °C before further chemical analysis.

The air quality at the sampling location is mainly influenced by particulate emissions from on-road traffic, nearby petroleum and chemical industries, ships from the nearby port and sea spray. Other than the local urban emissions, the ambient air quality in Singapore is also deteriorated occasionally by the transboundary smoke haze events caused by forest and peat fires in Indonesia as revealed by a number of previous studies (e.g., Balasubramanian et al., 1999; Betha et al., 2014; Orlic et al., 1999).

2.2. Bioaccessibility assessment and kinetic study

Altogether 6 haze samples and 12 non-haze $PM_{2.5}$ samples were selected for this study. Each quartz filter laden with $PM_{2.5}$samples was split into two halves. One half was used for determination of the total concentration of TrElems. An acid-aided (4 mL HNO_3 + 2 mL H_2O_2 + 0.2 mL HF) microwave digestion method was used. The details of the extraction method are described elsewhere (Betha and Balasubramanian, 2013; See and Balasubramanian, 2008). For assessment of the bioaccessibility of TrElems, ALF and the Gamble's solution were freshly prepared using analytical grade chemicals and MilliQ water (Millipore, 18.2 MΩ), kept in the incubator for 24 h before use (Midander et al., 2007). The other half of the quartz filters was exposed into 20 mL SLFs and kept in the incubator at 34 °C.9 $PM_{2.5}$ samples (3 haze + 6 non-haze) were extracted by each SLF. To conduct the dissolution kinetic study, 2 mL extract was taken using a pipette at each time point of 5 min, 10 min, 30 min, 2 h, 8 h, 1 day and 2 days after centrifuge at 10,000 rpm for 5 min, filtered and stored at 4 °C. The pH of the two extraction solutions was kept constant during the whole process (7.4 ± 0.8 and 4.5 ± 0.5 for Gamble's solution and ALF, respectively). All the extracts were stored at 4 °C before quantifying the amount of 13 elements (Al, As, Co, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, and Zn) using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (ELAN 6100 PerkinElmer, Inc., MA, USA.).

An appropriate standard reference material (SRM) (NIST SRM 1649a, urban particulate matter) was used to check the accuracy and recovery of the extraction method. The recoveries of the 13 elements ranged from 75% to 119%. Field blanks were also extracted and analysed along with filter samples. All the reported values have been corrected with deduction of the blank concentrations (roughly 10–20% of the total elemental concentration). Other quality control and quality assurance protocols were also strictly followed as reported in our previous publications (Betha et al., 2014).