



Assessment on the occupational exposure of urban public bus drivers to bioaccessible trace metals through resuspended fraction of settled bus dust

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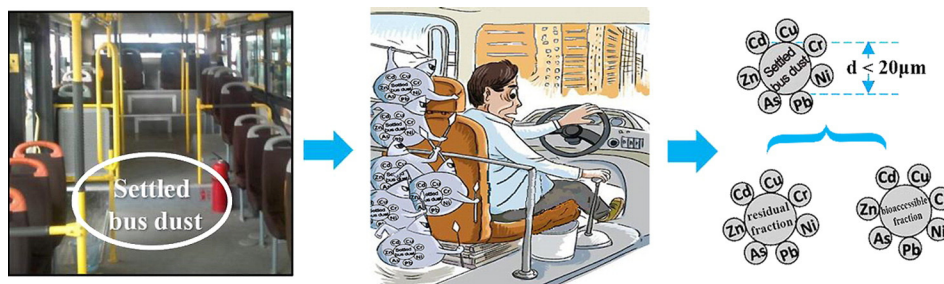
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HIGHLIGHTS

- As, Cd and Ni had relatively higher bioaccessibility and mobility in the resuspended fraction of settled bus dust.
- Bioaccessible metal concentrations were higher in gasoline-fueled buses than those in CNG-fueled buses.
- The carcinogenic risk probabilities to drivers were around the acceptable level.

GRAPHICAL ABSTRACT



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ABSTRACT

Limited information is available on the bioaccessible fraction of trace metals in the resuspended fraction of settled bus dust in order to estimate bus drivers' occupational exposure. In this study, 45 resuspended fraction of settled dust samples were collected from gasoline and compressed natural gas (CNG) powered buses and analyzed for trace metals and their fraction concentrations using a three-step sequential extraction procedure. Experimental results showed that zinc (Zn) had the greatest bioaccessible fraction, recorded as an average of 608.53 mg/kg, followed in order of decreasing concentration by 129.80 mg/kg lead (Pb), 56.77 mg/kg copper (Cu), 34.03 mg/kg chromium (Cr), 22.05 mg/kg nickel (Ni), 13.17 mg/kg arsenic (As) and 2.77 mg/kg cadmium (Cd). Among the three settled bus dust exposure pathways, ingestion was the main route. Total exposure hazard index (HI_T) for non-carcinogenic effect trace metals was lower than the safety level of 1. The incremental lifetime cancer risk (ILCR) for drivers was estimated for trace metal exposure. Pb and Ni presented relatively high potential risks in the non-carcinogenic and potentially carcinogenic health assessment for all drivers. ILCR was in the range of $1.84\text{E}-05$ to $7.37\text{E}-05$ and $1.74\text{E}-05$ to $6.95\text{E}-05$ for gasoline and CNG buses, respectively.

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1. Introduction

Dusts in the air whose particle sizes are less than $75\text{ }\mu\text{m}$ will deposit at the surface owing to their own weight, and then can resuspend and

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remain in the air for a long time because of the natural wind and human activities (ISO, 1994; IUPAC, 1990). Airborne and resuspended dusts carrying trace metals can impose adverse effects on human health via various non-dietary pathways (Shi et al., 2011; Luo et al., 2011; Lu et al., 2011; Komarek et al., 2008). The trace metals contained in the dust from the air as well as the urban road surface are mainly originated from the fuel combustion (Richter and Howard, 2000; Karavalakis et al., 2010). Different fuel resources directly result in different distributions of trace metals in surrounding road environment, which consists of macroenvironment, including air and road surface dust, as well as micro-environment such as transportation tool.

Buses are still an important integral part of urban transportation tool. The interplay exists between macro- and microenvironment by passengers' activities and ventilation, which result in the road dust and airborne dust introduced into buses. Airborne dust and resuspended fraction of settled bus dust can easily adhere to hands by dermal contact, then it can be subsequently ingested by hand-to-mouth contact and/or enter the respiratory system by inhalation (Brauer et al., 2002; USEPA, 2009). After the entrance into the human body, toxic metals interfere with the normal functions of the internal organs, disrupting the nervous system or endocrine system, or acting as auxiliary factors of other diseases (Zheng et al., 2010a, 2010b; Tang et al., 2013). Wang (1999) proposed that in vitro dissolution in a simulated lung fluid, due to long retention time of the toxic metal particles, toxic metal directly from the particles contributes over 90% of the absorbed dose to lung. Water-soluble metal chemicals can access into the blood stream via the hair follicle, sebaceous gland, and sweat gland. For example, about 1–6% of Cr can be absorbed by the digestive tract; 10–40% amount of Cr can be absorbed by the respiratory tract (Shi, 2002; Meng, 2003). When Cr enters into the blood stream, it tends to be mainly bounded with low molecular weight plasma protein and then be distributed in the kidney (about 30%) as well as the liver (about 16%) with the blood flow. The concentration of Cr is the highest in the hair. The absorption of Cr (III) by the digestive tract is less than 3%. In comparison, Cr (VI) is much easily absorbed in the digestive tract. The absorption of Cr (VI) by the respiratory tract is about 40%. After absorbed by the sweat gland of the skin, Cr (VI) reduces to Cr (III) in the dermis (Shi, 2002; Meng, 2003). As can be completely absorbed by their respiratory tract and be partially absorbed by the skin (Shi, 2002; Meng, 2003). Thus trace metal pollutants in airborne dust and resuspended fraction of settled dust pose a detrimental risk to the human beings' health, particularly to drivers due to their longer exposure time. However, accurate evaluation of the health risk of these metals is a pressing challenge for environmental researchers (Li et al., 2013a, 2013b; Kurt-Karakus, 2012; Cheng and Liao, 2012). Previous studies have used a comparison of total metal concentrations as an indicator to assess the safety levels and environmental risks of trace metals contained in urban dusts (Shi et al., 2011; Wang and Qin, 2007; Ferreira-Baptista and De Miguel, 2005). An overestimation of the risk seems to be present because of a failure to provide sufficient information about the bioaccessible trace metals, which are related to the toxicity, route of intake, bioaccessible kinetic inside the human body (Luo et al., 2011; Perez et al., 2008).

The bioaccessible trace metals, greatly depends on their existing forms. A three-step sequential extraction has been widely applied to assess trace metal speciation in solid matrices, namely water-soluble, exchangeable, carbonate-associated, iron (Fe)/manganese (Mn) oxide-associated, organic-associated or residual fractions (Rauret et al., 1999; Li et al., 2013a, 2013b; Bakircioglu et al., 2011; Feng et al., 2009; Fernandez et al., 2004; Pueyo et al., 2008; Zhang and Wang, 2009). Among these different forms, water-soluble and exchangeable fractions are considered to be bioavailable; carbonate-associated, Fe/Mn oxide-associated and organic matter-bound fractions can be also bioavailable depending on the pH transition and redox potential of urban soil/dust. Most residual fractions are non-bioavailable.

By the end of 2012, in Harbin, China, 70% of the city buses had been converted to run on compressed natural gas (CNG), while the rest were

still using gasoline as a fuel resource. Thus the potential effect of this conversion on public health required a comprehensive evaluation. The main aims of this study were to (1) study the chemical speciation and mobility potential of trace metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) in the resuspended fraction of settled bus dust using the three-step sequential extraction method; and (2) evaluate the risk of exposure to these trace metals for drivers working on buses fueled with gasoline and CNG, via inhalation, ingestion as well as dermal contact pathways.

2. Materials and methods

2.1. Sample analytical procedure

Settled bus dust samples were collected by vacuum cleaner (Philips FC6130) from the microenvironment of buses when no rain had occurred in the previous week. This was the main method employed to sample 45 settled bus dust from 45 bus routes in Harbin, capital and the largest city of Heilongjiang Province, China. Settled dust samples were collected from the PVC plastic floor in the front, middle and back sections of the buses in the bus station after one round operation. The settled bus dust samples were air-dried at room temperature and sieved to a mesh size less than 20 μm in order to get the resuspended fraction of settled bus dust. The 45 bus routes were grouped according to the two engine types, with 24 fueled with gasoline and 21 fueled with CNG, to investigate the impact of fuel type on the health risks posed by trace metals to drivers. About 50 mg of the resuspended fraction of settled bus dust samples was digested using the United States Environmental Protection Agency (USEPA) Method-3050B to measure the total amount of trace metals (USEPA, 1996). After digestion, trace metal analysis was conducted by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). Calibration standards were prepared daily by serial dilution ranging from 100–1000 $\mu\text{g/L}$ obtained from multiple dilutions of a multi-element calibration standard (Agilent Scientific Technology Ltd., USA). Three replicates of each sample were prepared for extraction and analysis, along with blank samples. The relative standard deviation of triplicate samples was routinely 2–4%. The relative error of standard reference materials was less than 4% (average value of the following metals was: As, 20.20 ± 0.83 ; Cd, 198.00 ± 5.67 ; Cr, 206.65 ± 1.70 ; Cu, 198.84 ± 7.73 ; Ni, 197.81 ± 6.23 ; Pb, 202.23 ± 6.74 and Zn, 202.77 ± 8.24). The instrumental detection limits were: As, 4.30 $\mu\text{g/L}$; Cd, 0.70 $\mu\text{g/L}$; Cr, 2.70 $\mu\text{g/L}$; Cu, 50 $\mu\text{g/L}$; Ni, 22.00 $\mu\text{g/L}$; Pb, 9.10 $\mu\text{g/L}$; Zn, 7.00 $\mu\text{g/L}$. The three-step sequential extraction procedure was used to separate the trace metals into four operationally defined fractions: acid-soluble/exchangeable fraction, denoted as F1; reducible fraction, denoted as F2; oxidizable fraction, denoted as F3; and residual fraction, denoted as F4 (Quevauviller et al., 1997). Summary procedures of this method are shown in the supplementary content. Extractions were performed in Teflon vessels with an end-over-end shaker rotated at 30 rpm. After each successive extraction, separation was done by centrifugation at 4000 rpm for 20 min. The supernatant was filtered and acidified to pH < 2 and then refrigerated until analysis for concentrations of different trace metals.

The bioaccessible trace metal is the sum of F1, F2 and F3 of those trace metals. The bioaccessible trace metal is often considered to be the direct and potentially hazardous fraction for organisms, because of their much weaker binding to solid sample compared with F4 (residual fraction–inactive fraction) (Bruder-Hubscher et al., 2002; Delgado et al., 2011; Tokalioglu and Kartal, 2006).

2.2. Recovery

An internal check was performed on the results of the sequential extraction by comparing the total amount of trace metals extracted by different reagents during the sequential extraction procedure with the results of the total digestion. The recovery of the sequential

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