Atmospheric Environment 119 (2015) 1–10

Contents lists available at ScienceDirect

Atmospheric Environment

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

Chemical speciation, human health risk assessment and pollution level of selected heavy metals in urban street dust of Shiraz, Iran

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HIGHLIGHTS

- This study assesses a comprehensive environmental risk of urban trace metal pollution.
- This study evaluates mineralogy and human health risk combined with the speciation of trace metals.
- Calcite, dolomite and quartz are main mineralogical components of dust.
- This study points the critical contaminated metals that need to be paid special attention.

ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form
31 July 2015
Accepted 1 August 2015
Available online 5 August 2015

Keywords:
Street dust
Potentially toxic metals
Modified BCR sequential extraction
Human health risk
Shiraz

ABSTRACT

The distribution, pollution level, sources and health risk of Hg, As, Cd, Cu, Cr, Ni, Mn, Fe, Pb, Sb and Zn in urban street dust were investigated. X-ray diffraction analysis of dust samples shows that the mineralogy of airborne dusts is dominated by calcite, dolomite and quartz. The total concentration of trace elements across the sampling sites ranged from 36.8 to 234.3 mg kg^{-1} for Pb, 0.004–4.504 mg kg^{-1} for Hg, 160.9–778.3 mg kg^{-1} for Zn, 245–652 mg kg^{-1} for Mn, 39.4–117.9 mg kg^{-1} for Ni, 31.6–105.9 mg kg^{-1} for Cr, 49.8–232.5 mg kg^{-1} for Cu, 5.3–8.6 mg kg^{-1} for As, 0.31–0.85 mg kg^{-1} for Cd, 0.76–9.45 mg kg^{-1} for Sb, and 16,300–24,900 mg kg^{-1} for Fe. The enrichment factor results reveal the following order: Cu > Hg > Sb > Zn > Pb > Ni > Cr > As > Mn > Cd > Fe. Among the measured elements, the highest mobility factor belongs to Pb (79.2%), Hg (74.6%), Zn (64.1%) and Mn (56.4%). According to the calculated Hazard Quotient (HQ) and Hazard Index (HI), special attention should be paid to Hg, Pb, Zn, and Mn in the street dusts of Shiraz. Multivariate statistics indicate that traffic, natural soil particles and industrial activities are likely to be the main sources of heavy metals in Shiraz street dusts.

1. Introduction

At present, over half of the global population lives in urbanized areas (United Nations, 2012). Rapid urbanization and intense human activities have made cities a focus of resource consumption, as well as chemical emissions and waste disposal resulting in a variety of environmental problems, including the major issue of potentially toxic metal pollution (Charlesworth et al., 2010). Street dust, the accumulation of solid particles on outdoor ground surfaces (Al-Khashman, 2007), is a valuable medium for characterizing urban environmental quality. Road dust originates from natural sources (e.g. re-suspension of soil and weathered materials) and various anthropogenic activities (e.g. vehicular traffic, industrial plants, power generation facilities, residential fossil-fuel burning, and construction and demolition activities) (Lu et al., 2009). Urban dusts have a high surface area and are easily transported and deposited, carrying a potentially toxic element load (Irvine et al., 2009). In recent years, many studies on street dust have focused on elemental contents (Liu et al., 2014). Among them, As, Cd, Cu, Cr, Hg, Ni, Pb, Sb, Sr, Pt and Zn are of particular concern (Shi et al., 2011). Road dust, particularly the fine particles, can be absorbed by humans through ingestion, inhalation and dermal adsorption (Wei et al., 2010). Health risk is especially high for children because of their low tolerance to toxins as well as their inadvertent ingestion of significant quantities of dust through hand-to-mouth pathways (Acosta et al., 2009). While numerous studies of heavy metal contamination of street dust have been carried out in

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http://dx.doi.org/10.1016/j.atmosenv.2015.08.001
1352-2310/

developed countries (Elom et al., 2014), only limited information is available on heavy metals of street dust in developing countries, including Iran. Saeedi et al. (2012) found that traffic and related activities, petrogenic and pyrogenic sources are likely to be the main anthropogenic sources of heavy metals and PAHs in Tehran street dust. Furthermore, Gholampour et al. (2014) evaluated the exposure and health impacts of outdoor particulate matter in two urban and industrialized areas of Tabriz.

Shiraz, experiencing a rapidly growing population in the last decades, is polluted by heavy traffic, residential heating, small industries and workshops. In recent years, particulate matters coming from western neighboring countries have drastically increased in western and even central parts of Iran. Even though there is no confirmed origin, it is suspected that most of this dust originates from the dried wetlands of southeastern Iraq and the deserts of Iran's western neighbors (Bashiri Khuzestani and Souri, 2013). With severe dry deposition and dust settling in the area, no known study has been conducted nor reported on the environmental quality of the street dust of Shiraz.

In summary, the main purposes of this study were to (1) evaluate the degrees of concentration of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn, and Hg in urban street dusts from different areas of Shiraz, a typical big city in the southwest of Iran; (2) investigate the chemical speciation and mobility potential of these elements using the modified BCR sequential extraction method; and (3) assess the human health risk of these metals to both children and adults via inhalation, ingestion as well as dermal contact.

2. Materials and methods

2.1. Study area

This study was conducted in Shiraz, the capital city of Fars province, the fifth populated city in Iran with 223.4 km^2 and located at latitude of 29°37′8″ N and longitude of 52°31′14″ E (Maharlouei et al., 2013) (Fig. 1). The population in the Municipality of Shiraz has been estimated to be 1,749,926 inhabitants in 2011 Statistical Center of Iran (2011) with average density of 7833 persons/km^2. The annual mean temperature, precipitation and weed speed are 18.6 °C, 325.6 mm and 2.35 m s^{-1}, respectively (IRIMO, 2010). The prevailing wind directions in the Shiraz meteorological station are west to east and northwest towards southeast (IRIMO, 2010). According to the report of Shiraz traffic organization, the number of vehicles and auto-rickshaws (two-stroke engine vehicles) passing through the city from 250,000 in 2007 reached to 700,000 in 2014 (Office of Transport and Traffic Shiraz Municipality, 2014). Gaseous wastes in the form of automobile exhaust and factory chemicals, as well as from primitive forms of heating, are the major sources of air pollution in the country. In addition to high population growth, the rate of urbanization has also accelerated, and is now one of the highest in Iran.

2.2. Sampling, sample preparation and chemical analysis

A total of 21 street dust samples were collected on the driest month of the year (August 2013). The sampling sites were roughly distributed all over the urban areas (Fig. 1). Road characteristics, land use near the sampling sites, and geographic coordinates were recorded. At each site, about 300 g of dust present on impervious surfaces (road, pavement) within an area of 2–10 m^2 were collected using polyethylene brushes. All samples were stored in sealed polyethylene bags, labeled and then transported to the laboratory. After air-drying, the coarse impurities of the samples such as stone, cigarette butt, plastic and leaves were removed; and then all the rest was grounded with an agate mortar and pestle to be passed through a 63 μm (220 mesh) nylon sieve. The mineralogy of dust samples was determined using X-ray diffraction (XRD) at the geological survey of Tabriz, Iran. For this purpose, samples were ground using a Tema Grinder and a Siemens D 500 diffractometer. Total concentration of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Zn, and Hg were measured using inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN 9000) at the accredited Acme Analytical laboratory, Canada. For the analysis of heavy metals, a wet digestion procedure was adopted from Qi and Grégoire (2000). Number of analyses in this study is 47 including 6 mineralogical analyses, 20 fractionation analyses and 21 heavy metals analyses.

Quality control and quality assessment included reagent blanks, analytical duplicates and analysis of the standard reference material (multi-element soil standard OREAS45EA and OREAS24P). The recovery percentages are As (94.2%), Hg (88.6%), Cr (89.5%), Cu (99%), Mn (91.8%), Ni (93.3%), Pb (106.4%), Zn (92.5%), Cd (105.3%), Fe (90.7%) and Sb (85.2%) indicating a good agreement between the measured and the certified values.

2.3. Pollution assessment methodology

The enrichment factor (EF) method described by Sutherland (2000) was used to evaluate the potential impact of the dust samples. The EF of each element, which is a normalization of an element of interest against a reference one, was calculated using the following equation:

$$EF = \left(C_n / C_{ref}\right)_{sample} \Big/ \left(B_n / B_{ref}\right)_{background} \quad (1)$$

Here (C_n/C_{ref}) is the ratio of concentrations between heavy metal and a reference metal in the sample and background. In this study, the reference metal was selected based on the correlation coefficient analysis and on previous works. The reference metal chosen is neither likely to be affected by anthropogenic activities nor correlated with heavy metal pollutants. The EF was split into five classes as follows (Yongming et al., 2006): EF < 2, class 1, deficiency to minimal enrichment; 2 ≤ EF > 5, class 2, moderate enrichment; 5 ≤ EF > 20, class 3, significant enrichment; 20 ≤ EF > 40, class 4, very high enrichment; and EF ≥ 40, class 5, extremely high enrichment.

The method of determining ecological risks of heavy metals originally introduced by Hakanson (1980) has recently been used in dust contamination studies (Tang et al., 2013). Hence, the potential ecological risk index (PERI) was calculated to assess the degree of metal pollution in Shiraz street dusts as follows:

$$RI = \sum_{i=1}^{m} Er \quad (2)$$

$$E_r = T_r \times C_f \quad (3)$$

$$C_f = \frac{Cs}{Cn} \quad (4)$$

where C_s and C_n are heavy metal sample and background concentrations, respectively, E_r is the ecological risk of each element and RI shows the ecological risk of multiple elements. Hakanson (1980) defined T_r as a "toxic-response factor" for a given substance and demonstrated this value for Hg, Cd, As, Cu, Pb, Ni, Cr, Zn, Mn to be 40, 30, 10, 5, 5, 5, 2, 1, 1, respectively. The following terminologies are used to describe risk levels: $E_r^i < 40$, low potential ecological risk; $40 \le E_r^i < 80$, moderate potential ecological risk; RI < 150, low ecological risk; 150 ≤ RI < 300, moderate ecological risk; 300 ≤ RI < 600, considerable ecological risk; and RI ≥ 600, very