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Chemical fractionation of arsenic and heavy metals in fine particle matter and its implications for risk assessment: A case study in Nanjing, China

Huiming Li [a], Jinhua Wang [a], Qin'geng Wang [a], Xin Qian [a, *], Yu Qian [a, *], Meng Yang [b], Fengying Li [b], Hao Lu [a], Cheng Wang [a]

[a] State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210023, China
[b] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

HIGHLIGHTS

- The fractionation distribution pattern and mobility differed among metals in $PM_{2.5}$.
- Zn, As, Cd, Cu, and Ni showed high environmental risk and Pb showed a medium risk.
- Human carcinogenic risk from metals in $PM_{2.5}$ was higher than accepted criterion.
- The non-carcinogenic human health risk was lower than but close to the safe level.

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ABSTRACT

A four-step sequential extraction procedure was used to study the chemical fractionation of As and heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in fine particulate matter ($PM_{2.5}$) collected from Nanjing, China. The mass concentrations of most $PM_{2.5}$ samples exceeded the 24 h standard (75 μg/m^3) recommended by the new national ambient air quality standard of China. The most abundant elements were Fe, Zn and Pb, while As and Cd were present at the lowest concentrations. As, Cd, Cu, Mn, Pb and Zn were mostly present in the two mobile fractions, including the soluble and exchangeable fraction (F1), and carbonates, oxides and reducible fraction (F2). Fe had the highest proportion present in the residual fraction (F4). Relatively high proportions of the metals Ni and Cr were present in the oxidizable and sulfidic fraction (F3). High proportions of Zn, As and Cu and lower proportions of Cd, Cr and Fe were present in the potentially mobile phases. The enrichment factor, contamination factor and risk assessment code were calculated to analyze the main sources and assess the environmental risks of the metals in $PM_{2.5}$. The carcinogenic risks of As, Cd, Ni and Pb were all lower than the accepted criterion of 10^{-6}, whereas the carcinogenic risks of Cr for children and As and Cr for adults were higher than 10^{-6}. The non-carcinogenic health risk of As and heavy metals because of $PM_{2.5}$ exposure for children and adults were lower than but close to the safe level of 1.

1. Introduction

Urban atmospheric pollution is a serious environmental issue that has arisen from the rapid economic development in megacities. Among the atmospheric particulate matter (PM), fine particulate matter with an aerodynamic particle diameter of ≤2.5 μm ($PM_{2.5}$) is of concern because of its adverse health effects and close association with haze (Sun et al., 2006; Jiao et al., 2012). Besides particle concentration and size distribution, the chemical composition is also crucial to the toxicity of PM (Louie et al., 2005; Xie et al., 2012). Metal compounds are an important class of PM. It is well known that $PM_{2.5}$ has high concentrations of many potentially toxic metals that can be incorporated into the human body through inhalation and have adverse physiological effects (Mohanral et al.,

* Corresponding authors.
E-mail addresses: xqian@nju.edu.cn (X. Qian), yqian@nju.edu.cn (Y. Qian).

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2004). Additionally, metal elements absorbed to PM in the atmosphere may travel long distances and be deposited to soils, water bodies, and plant leaves via wet and dry deposition, which poses a potential risk to the local environment (Li et al., 2013b).

It is generally recognized that the chemical fractionation of a metal determines its mobility, bioavailability and the potential risks it poses to the environment and to human health (Fernández Espinosa et al., 2002; Pérez et al., 2008; Schleicher et al., 2011). The mobile or labile fraction of a particle-bound metal is considered to be more available to environmental receptors and more hazardous to organisms than a resistant fraction. Sequential extraction methods have been widely applied to characterize the chemical forms of metal elements present in various environmental samples, including soils (Kaasalainen and Yli-Halla, 2003; Davidson et al., 2006), river and marine sediments (Ayyamperumal et al., 2006; Arain et al., 2008), sludges (Fuentes et al., 2004; Yuan et al., 2011), street dusts (Tokaliolu and Kartal, 2006; Li et al., 2013a), and atmospheric particles (Fernández Espinosa and Ternero Rodríguez, 2004; Schleicher et al., 2011). These methods can be used to estimate the differentiation of relative bonding strength of metals in various solid phases and their potential reactivity under different physicochemical environmental conditions (Yuan et al., 2011). There are several sequential chemical fractionation schemes available for PM, and these are based on the sequential extraction procedure (SEP) reported by Tessier et al. (1979), the BCR sequential extraction procedure from the European Community's Bureau of References (Ure et al., 1993), Chester's procedure (Chester et al., 1989), and Zatka's procedure (Zatka et al., 1992). In this study, a four-step modified Tessier scheme developed by Fernández Espinosa et al. (2002) was used. This procedure has been used in several studies for fractionating fine PM-bound metals and evaluating their mobility and bioavailability (Fernández Espinosa and Ternero Rodríguez, 2004; Sammut et al., 2006; Gómez et al., 2007; Feng et al., 2009; Schleicher et al., 2011).

Many studies have shown that heavy metal concentrations in $PM_{2.5}$ in big cities in China are often well above natural background levels because of anthropogenic effects such as industrial activities and traffic emissions (Li et al., 2013b). However, most of these studies have used comparisons of total metal composition in $PM_{2.5}$ to determine the pollution conditions and have not considered the metal fractionation. There are very few reports about the fractionation distribution and risk assessment of heavy metals in $PM_{2.5}$ from cities in China and other countries. Therefore, the main objectives of this study were to study the chemical fractionation distribution of As and heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in $PM_{2.5}$ collected from different areas of Nanjing, which is a typical mega-city in China, and to evaluate the mobility potential and environmental risk based on the metal fractionation distribution and human health risk via inhalation of $PM_{2.5}$.

2. Materials and methods

2.1. Sampling collection

Nanjing (118°46′E, 32°03′N), the capital of Jiangsu province in Southeastern China, has a total area of approximately 6600 km^2, and had a population of >8.1 million in 2012. Nanjing has a north subtropical monsoon climate and the prevailing wind is from the southeast in summer and the northwest in winter. Its average annual temperature is 16 °C and average annual precipitation is 1106 mm. Nanjing is an important industrial production area and is the main transportation hub in East China.

$PM_{2.5}$ samples were collected from the two different areas of Nanjing, at Xianlin Campus and Gulou Campus of Nanjing University (Fig. 1). The Xianlin campus of Nanjing University, which is in the educational district, is located in the northern suburbs of Nanjing and near the northern industrial zone of Nanjing. The Gulou campus of Nanjing University, which is in the commercial/residential district, is located in the center of the city and near the central business area of Nanjing. $PM_{2.5}$ samples were collected on quartz microfiber filters (20.3 cm × 25.4 cm, Whatman International Ltd., Maidstone, England) using high-volume PM samplers

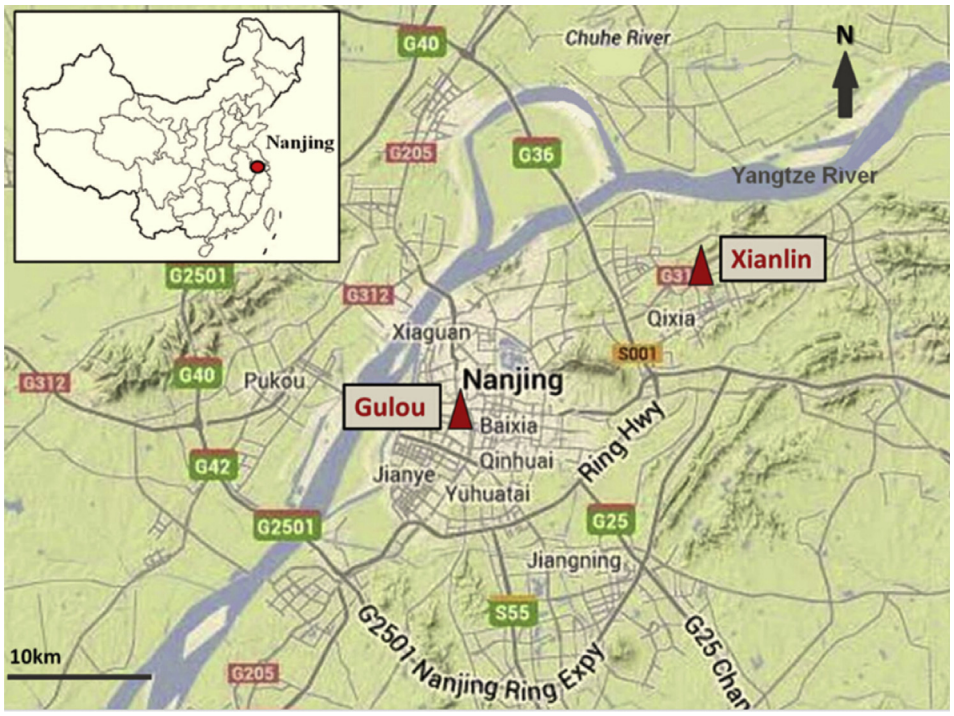

Fig. 1. $PM_{2.5}$ sampling sites at Nanjing University (China) campuses in Xianlin and Gulou.