Speciation of heavy metals in airborne particles, road dusts, and soils along expressways in China

SHAO Li¹, XIAO Huayun², and WU Daishe¹

¹ Environmental and Chemical Engineering College, Nanchang University, Nanchang 330031, China
² State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

* Corresponding author, E-mail: shaoli@ncu.edu.cn

Received May 8, 2012; accepted June 8, 2012
© Science Press and Institute of Geochemistry, CAS and Springer-Verlag Berlin Heidelberg 2013

Abstract This study analyzed the concentrations and chemical forms of Zn, Cu, Pb, Sb, Cd and Mn in airborne particles, road dusts and soils collected along three expressways in Jiangxi Province, China, with different traffic densities, and identified the levels and sources of heavy metal contamination. The concentrations of Zn, Cu, Pb, Sb, and Cd except Mn in airborne particles, road dusts and soils were all in direct proportion to traffic volume. Cd concentrations were low compared with other metals. For instance, the concentrations of Zn, Cu, Pb, Sb, Mn and Cd were 6.6, 0.7, 2.2, 0.1 and 0.1 μg·m⁻³ in PM10 along the Changjiu Expressway, 792.8, 241.4, 248.3, 9.6, 340.5 and 8.0 mg·kg⁻¹ in road dusts, and 201.1, 143.2, 59.5, 9.5, 338.9 and 2.3 mg·kg⁻¹ in soils, respectively, but in the case of the ratio of concentration to the environmental background value, most serious contamination was caused by Cd. The sources of the heavy metals were judged by comparisons of the chemical forms of the heavy metals in different environmental media. Pb and Mn in airborne particles were both derived from traffic; Pb in road dusts and soils resulted mainly from the use of leaded gasoline in the past; and Mn in road dusts and soils was derived from parent rocks. Zn, Cu, Sb and Cd in airborne particles, road dusts and soils were derived primarily from traffic, and differences in chemical forms of heavy metals in different media were due to the interaction between heavy metals in airborne particles and organic matter and other surfaces in road dusts and soils. We also discussed the change of chemical forms of heavy metals in particles of different sizes and under different weather conditions. Bioavailability of heavy metals in airborne particles was much higher than that in road dusts and soils, especially Pb (0.676 in airborne particles, 0.159 in road dusts and 0.095 in soils).

Key words expressway; airborne particle; road dust; soil; heavy metal; traffic

1 Introduction

Road traffic is recognized as an important source of heavy metals. Traffic-related heavy metals such as Zn, Cu, Sb, Pb, Mn, Cd and Ni mainly come from automobile exhausts and the wear of tires, brake linings and bearings (Harrison, 2003; Trang, 2011; Miguel, 1997; Sternbeck, 2002). There is more evidence suggesting that metals may play a role in autoimmune diseases such as Type-1 diabetes, multiple sclerosis, systemic lupus erythematosus, rheumatoid arthritis and Alzheimer's disease (Forte, 2005; Kozlowski, 2009; Lawrence and McCabe, 2002). Mobility and bioavailability of heavy metals are decided not only by total metal contents, but also by their geochemical forms. It is necessary to study contaminative and geochemical characteristics of vehicle-derived heavy metals since China has become the second largest country with respect to its number of car ownership.

A study had been conducted on the concentrations of a range of inorganic elements at a roadside location in Birmingham, UK (Harrison, 2003). Mn, Cu, Zn, Mo, Ba and Pb in PM10 showed the strongest correlation with NOₓ, which indicated that these metals mostly originated from traffic. Sezgin (2003) found that there was heavy metal pollution in the inspected area along E-5 Highway in Istanbul. Sternbeck (2002) measured particle emissions in two heav-
ily trafficked tunnels in Sweden, and concluded that the vehicle-derived metals (Cu, Zn, Cd, Sb, Ba and Pb) were mainly derived from wear rather than from combustion. Han Dongyu (2004) thought that the accumulation of Cu, Pb and Zn in road dusts in representative parks in Beijing may come mainly from traffic sources.

A number of previous studies were conducted on the distribution of heavy metals in road dusts and soils in China (Zhang Huifeng, 2010; Guo Guanghui, 2007; Han Dongyu, 2004; Chen Tongbin, 2004; Li Bo, 2005; Chen Xi, 2010). However, these studies focused only on the distribution characteristics of heavy metals. In addition, the chemical forms and transformation of heavy metals in airborne particles, road dusts and soils were seldom dealt with in the past.

The aim of the present investigation is to analyze the chemical fraction, study transport and transformation in the system of airborne particles-road dusts-soils, and to evaluate contamination levels and ecological risk of heavy metals.

2 Materials and methods

2.1 Sample collection and pretreatment

There was a great difference in traffic volume among the Changjiu (CJ) Expressway (from Nanchang to Jiujiang, Jiangxi Province, China), the Changzhang (CZ) Expressway (from Nanchang to Zhangshu, Jiangxi Province, China), and the Wenhou (WH) Expressway (from Wenjiazhen to Houtian, Jiangxi Province, China), which is conducive to research on the contamination characteristics of traffic-related heavy metals. Data on monthly traffic volume were listed in Table 1.

Airborne particles of different diameters (PM$_{10}$, 10 µm $<$ Da50 $\leq$ 100 µm and TSP) were collected during April to June, 2009 along the Changjiu Expressway and Changzhang Expressway, and in the countryside far away from the expressways with TSP high volume (1.05 m$^3$·min$^{-1}$) and samplers with PM$_{10}$ cutting head. The samples were collected on mixed cellulose ester mollipore filters for sequential 24-h intervals over a ten-day period at each sampling site. All filters were previously soaked overnight in 10% nitric acid, rinsed with distilled water, dried in a vacuum drier, and put into sealed polythene bags.

Road dust and topsoil samples were collected along the Changjiu, Changzhang, and Wenhou expressways in April 2012. A clean plastic brush was used to whisk road dust onto a clean paper and the samples were placed in sealed polythene bags. Surface soil samples at the depth of 0–10 cm adjacent to road surfaces were collected using a stainless steel shovel from transects parallel to the road at 3–4 m away from the kerb, and put into sealed polythene bags, too. The road dust and soil samples were air-dried naturally in laboratory for about two weeks, then they were tapped lightly with a wooden mallet and sieved through a 20-mesh polyethylene sieve (<0.8 mm) to remove stones, coarse materials and other debris, and dried to a constant mass in a dryer at 75°C.

In order to research the chemical speciation of heavy metals in road dusts of different sizes, the road dusts were sieved through a 0.1-mm nylon mesh sieve into two fractions: Da50 $>$ 100 µm and Da50 $\leq$ 100 µm.

The sampling sites are shown in Fig. 1.

2.2 Chemical analysis

2.2.1 Total elemental analysis

One quarter sampled filter and road dust and soil samples (250 mg) were digested with an acid mixture containing 2 mL HNO$_3$, 6 mL HCl and 1 mL HF. Hydrofluoric acid was added to avoid the precipitation of silicates. After digestion, Zn, Cu, Sb, Pb, Mn and Cd were analysed by ICP mass spectrometry. The detection limits for Zn, Cu, Sb, Pb, Mn and Cd were 0.020, 0.049, 0.008, 0.013, 0.038 and 0.020 µg·L$^{-1}$, respectively.

Precision and accuracy of all the methods were determined by analyzing standard reference materials (GBW07405) obtained from the Center of National Standard Reference Material of China. Analytical precision of all the methods, measured as the relative standard deviation (RSD), is generally lower than 0.1, while the analytical accuracy, measured as the logarithmic deviation ($\Delta$lgC), is generally lower than 0.03.

<table>
<thead>
<tr>
<th>Road</th>
<th>Traffic volume (vehicle)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Car</td>
<td>Truck</td>
</tr>
<tr>
<td>Changjiu Expressway</td>
<td>1109124</td>
<td>337637</td>
</tr>
<tr>
<td>Changzhang Expressway</td>
<td>237988</td>
<td>100153</td>
</tr>
<tr>
<td>Wenhou Expressway</td>
<td>38428</td>
<td>54921</td>
</tr>
</tbody>
</table>

Note: *Data from monthly traffic volume report from the website of Jiangxi Ganyue Expressway Co., Ltd. www.jxexpressway.com.