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Spatial distributions and characteristics of platinum group elements (PGEs) in urban dusts from China and India

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ABSTRACT

This study investigated platinum group elements (PGEs) in urban dusts from metro cities of China and India. The dust samples were collected during 2007 to 2009 and determined by inductively coupled plasma-mass spectrometry (ICP-MS). The PGE concentrations in the samples from China are within the range of 4.3 to 385 ng/g for Pt, 3.8 to 538 ng/g for Pd and 2.5 to 134 ng/g for Rh, respectively, and from Kolkata of India are within the range of 2.6 to 51.0 ng/g for Pt, 0.7 to 63.7 ng/g for Pd and 0.2 to 21.3 ng/g for Rh. The level of PGE concentrations is far higher than that of natural background, and this could be attributed to PGE catalytic converters used for automobiles. The PGE abundance levels in the urban dusts from individual cities are different and mainly reflective of the time length for PGE used as catalysts and density of vehicles equipped with catalytic converters. Despite the relatively shorter time period for catalytic converters applied to vehicles in China, PGE contents in the urban dusts from Beijing, Shanghai and Guangzhou have been up to the same magnitude as that in developed countries. According to the ratios of individual PGE to the total PGE contents (ΣPGE) in the urban dusts, the Pt–Pd–Rh catalytic products were found to have characteristics of varied proportions for both Pt/ΣPGE and Pd/ΣPGE, and relatively constant proportion for Rh/ΣPGE (e.g. constant proportion of (Pt + Pd)/ΣPGE). The varied proportions of Pt and Pd in catalyst products could imply that there have been some development and improvement of catalyst technology in developing countries. The PGE proportions indicate Rh is a minor component and Pt + Pd is a dominantly major component in the Pt–Pd–Rh catalytic products.

1. Introduction

Environmental scientists have been drawing much attention to the fast development of automobile industry due to its effect on urban environment. In order to control pollutant emission, platinum group elements (PGEs) as catalysts have been widely applied to automobiles. At present, the commonly used PGE catalysts are platinum (Pt), palladium (Pd) and rhodium (Rh). According to previous reports, there is a rapid growth in the amounts of Pd consumed by catalytic converters since 1990s, for example from 22 t in 1993 to 126 t in 2009 (Zereini et al., 2012), and more than 90% of the worldwide Rh supply were related to production of catalytic converters (Tuit et al., 2000). As a result, there is a rising trend in PGE abundances in urban environments compared with its natural levels in continental crust (Zereini et al., 2001). In the report of Rauch et al. (2004), the PGE deposition rate in an urban lake of Boston was found at 15, 8 and 5 folds higher for Pt, Pd and Rh, respectively than that before the usage of PGE catalysts.

Since mid-1970s when PGE catalytic converters were applied to vehicles in North America, there have been some changes in PGE converter products such as from the early Pt–Rh, and then Pd-rich to current Pt–Pd–Rh three-way catalysts (Cicchella et al., 2003; Zereini et al., 2007). These types of products also reflect the development process of catalytic technology to meet extremely strict emission legislation in developed countries such as U.S. and Europe (Barbante et al., 2001). In contrary to developing countries like China, autocatalysts have been used for a short time period, but the rapid increase in vehicle numbers has also consumed large amounts of PGE catalysts. For the largest developing countries like China and India, however, the investigations on the PGE abundances in urban environments are still not enough (Fang et al., 2005; Kan and Tanner, 2004, 2005; Pan et al., 2009; Qi et al., 2011; Wang and Sun, 2009; Wang et al., 2007; Yang et al., 2008). Therefore it is important to assess the effect of PGE catalysts related to vehicles on urban samples of the two countries.

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The objectives of the current study are: (1) to investigate the concentration and spatial distribution of PGE in street dusts from metro cities of China and India; and (2) to present the characteristics of PGE catalytic products used for automobiles in the metro cities of China.

2. Experimental

2.1. Sampling location

Considering the geophysical and economic conditions of Chinese cities in the present study, dust samples were collected from seven representative cities including Beijing, Guangzhou, Shanghai, Wuhan, Hong Kong and Macao as well as from Kolkata in India. Among these cities, the detailed information of Beijing, Guangzhou, Hong Kong, Macao, and Kolkata is available in our previous publication (Pan et al., 2009). Shanghai, located in eastern part of China is a famous financial city in the world, and had approximately 2.13 million vehicles at the end of 2006. This number ranks second in China being slightly less than that of Beijing. Wuhan in center of China is also one of the largest cities but has much less vehicles than that of Shanghai.

2.2. Sample collection

During 2007 to 2009, 59 dust samples were collected with a nylon brush for manually sweeping the road surface. These samples were air-dried and sieved through the bore diameter of <2 mm. After sieving, they were homogenized in sealed plastic bottles by shaking and stored for analysis.

2.3. Sample preparation and quality control

The whole procedure for analysis of PGE can be referred to the method of Sun and Sun (2005), who modified the conventional nickel sulfide fire assay. Following is an outline of the fire assay technique for preconcentration of PGE: each of the samples (5 g) was mixed with the flux of $Na_2B_4O_7$ (12 g), Na_2CO_3 (6 g), Fe (2 g), Ni (1 g) and S (1 g) and then fused at 1050 °C for 40 min. During the fusion, PGE was concentrated into a sulfide bead and therefore separated from sample matrix. The bead was then dissolved in HCl and some insoluble residue was left. The insoluble residue containing PGE sulfide was collected by filtration, and then dissolved using aqua regia for preparation of a resulting solution. The solution was kept for determination of Pt, Pd and Rh by inductively coupled plasma-mass spectrometry (ICP-MS). The recovery and reproducibility for the whole procedure were evaluated using the certified reference material of BCR-723, and the former was higher than 90% (92 ± 5% for Pt, 95 ± 3% for Pd and 96 ± 3% for Rh) and the latter was better than 5%.

3. Results and discussion

3.1. The concentrations and sources of PGE

As shown in Table 1, the PGE concentrations in dust samples from the cities of China are within the range of 4.3 to 385 ng/g for Pt, 3.8 to 538 ng/g for Pd and 2.5 to 134 ng/g for Rh, respectively. The highest PGE concentrations were found in Macao samples, with a geometric mean (GM) of 113 ng/g for Pt, 121 ng/g for Pd and 30.6 ng/g for Rh, respectively. The lowest PGE concentrations are in Wuhan samples with a GM of 22.8 ng/g for Pt, 16.1 ng/g for Pd and 7.5 ng/g for Rh, respectively. The PGE concentrations in the samples from Kolkata of India range from 2.6 to 51.0 ng/g (GM: 13.5 ng/g) for Pt, 0.7 to 63.7 ng/g (GM: 10.8 ng/g) for Pd and 0.2 to 21.3 ng/g (GM: 3.6 ng/g) for Rh. Compared with the PGE background values of 0.4 ng/g for Pt, 0.4 ng/g for Pd and 0.1 ng/g for Rh in continental crust (Wedepohl, 1995), the PGE abundances are significantly higher in urban dusts collected from the above mentioned cities of China and India (Table 1).

Table 1
Geometric mean (GM) and concentration ranges of measured PGE in urban dusts.

City	N	Pt/ng/g		Pd/ng/g		Rh/ng/g	
		Range	GM	Range	GM	Range	GM
China							
Beijing	10	12.3–84.6	45.2	10.1–131	41.3	3.5–30.6	14.7
Shanghai	8	7.9–54.9	22.0	32.1–178	111	5.1–26.4	15.0
Guangzhou	13	13.8–315	86.1	27.8–538	107	8.6–134	31.0
Qingdao	7	4.3–86.4	26.2	7.2–211	29.7	2.5–50.0	10.3
Wuhan	8	7.2–49.2	22.8	3.8–63.3	16.1	2.9–18.1	7.5
Hong Kong	7	35.5–268	112	59.4–307	125	11.4–68.4	23.9
Macao	9	28.4–385	113	31.4–472	121	7.6–88.0	30.6
Background	4		0.5		0.1		0.1
India							
Kolkata	10	2.6–51.0	13.5	0.7–63.6	10.8	0.2–21.3	3.6
Background	3		0.4		0.4		0.1

According to previous investigations, the PGE emission rate from autocatalytic converters to urban environment was found between 0.5–0.8 μg/km for Pt and 0.3–0.5 μg/km for Pd, respectively (Helmers, 1997; Tuit et al., 2000). Along with the wide application of automobile catalysts, the abundances of PGE in urban environments could become higher and higher. As a dominantly anthropogenic source, automobile PGE catalysts in automobile industry have been a significant effect on urban dusts.

For these dust samples, there exist significant correlations between individual PGE contents, and the correlation coefficients (R^2) are 0.483 for Pt and Pd, 0.787 for Pt and Rh, and 0.687 for Pd and Rh, respectively. Similar relationships have been observed for soil samples from the same cities of China and India (Pan et al., 2009), and further indicate that the effect of automobile catalysts on urban environments has been significant.

3.2. Comparison of PGE content levels

Among the metro cities, there are higher contents of PGE in the samples of Hong Kong and Macao. This is because Hong Kong and Macao were British and Portuguese colonies before 1997 and 1999, respectively and not only the same emission standards were employed as European countries but also catalytic converters were applied to vehicles as early as European countries. In addition, the two cities are characterized by narrow streets and high buildings, which make vehicle exhaust dispersion poor. Similar phenomenon was also noticed in the snow samples from Aspe Valley, in which the V-shaped valley was not suitable for vehicle exhaust to move for a longer distance (Moldovan et al., 2007). In mainland of China, Beijing, Shanghai and Guangzhou are the earliest cities, in which vehicles were equipped with catalytic converters. Beijing is the capital of China and possesses the highest numbers of vehicles but the PGE concentrations in its samples are relatively lower. The reason might be related to the sampling time of 2007, before 2008 Beijing Olympic Games. During the time period, there was a lot of engineering construction, releasing considerable dusts to dilute the contents of PGE in road dusts. Similar case was also reported for PGE data from two sampling sites in Austria because of road construction (Fritsche and Meisel, 2004). Among the three cities, the automobile number of Guangzhou is significantly lower than both of Beijing and Shanghai but the Guangzhou's dusts have the highest PGE contents (Table 1). This might be contributed to the fast increase in new automobiles, almost by 23% in 2007 due to motorcycles prohibition since 1st, Jan of the same year (http://www.gztpri.com/sitecn/Perper/4037.html). At that time, those new automobiles had to be equipped with catalytic converters due to the implementation of the related government rules. As a result, there is a higher percentage of autocatalysts applied to vehicles in Guangzhou. In addition, the climate of Guangzhou is warm and moist, and there are less street dusts than that in Beijing, resulting less dilution of Guangzhou's dust samples. Qingdao is not a