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PLATINUM CONCENTRATIONS IN URBAN AIRBORNE PARTICLES FROM SHANGHAI, CHINA

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ABSTRACT

The PM_{10} airborne particle samples were collected at Shanghai from December 2003 to December 2005 in order to investigate platinum contamination in the urban air. The samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The results show that the average Pt concentration in the air of the center of Shanghai was 1.69±0.93 pg m^{-3} that the increment of the Pt concentrations in Shanghai air was no significant from December 2003 to December 2005, and that the seasonal variations of the Pt concentrations over two years are possibly due to meteorological influences (i.e., wind and rain). The analytical results of the sixteen PM_{10} samples simultaneously collected at four sampling sites with different traffic intensity in Shanghai show a clear dependence between Pt concentrations and traffic intensity, which suggests that the auto exhaust is the main emission source of Pt in Shanghai air. Compared with the Pt background value of 0.54±0.03 pg m^{-3}, the Pt contamination in the ambient air of the center of Shanghai is significant. However, the Pt contamination level in Shanghai air is lower than one in urban air of some cities in Europe, the United States and Japan.

KEYWORDS: air pollution, aerosol particle, platinum, ICP-MS

1. INTRODUCTION

The United States, Canada, and Japan introduced cars with three-way catalytic converters in 1976 to reduce harmful atmospheric pollution from automobiles. Europe followed in the late 1980s. Element platinum plays a decisive role in the performance of the catalytic converters. However, the hot exhaust gases flowing through the catalytic converter cause abrasion and ablation of these units, leading to the broadcast of the Pt to the environment. Thus, the novel anthropogenic metal has an increasing impact on nature due to the increasing number of cars equipped with the catalytic converters (Zeneiri *and Alt*, 2000; Ravindra *et al.*, 2004). Moreover, several platinum group elements and their complex salts (e.g. Pt-and Pd-chlorides) have been reported as potential health risks to human, causing asthma, allergy, rhino-conjunctivitis and other serious health problems (Merget, 2000; Merget and Rosner, 2001). No data are as yet available about inhalation exposure, nevertheless, several observations identify a possible danger by inhalation (Arteit *et al.*, 2000; Köning *et al*., 1992). Considering the facts mentioned above, the monitoring of Pt originating from the emission of the automotive catalytic converters has very importance with respect to estimation of the future risk of the human health and the ecosystem. The monitoring the Pt concentrations is part of the environmental and health programmes of the IAEA and the WHO (WHO, 1991).

Shanghai is the largest city in the China with over 16.74 million people and 1.4 million automobiles up to 2005. Since 2002, the European Commission Vehicle Emissions Limits Standards has been implemented in Shanghai City, which means large numbers of the three catalytic converters have been applied to automobiles in this City. While a number of studies have provided Pt, Pd and Rh concentrations in airborne particulate matter in urban areas of Europe, United States and Japan, few studies have been performed in China. Here, the first study of Pt concentrations in urban airborne particles from Shanghai in China is reported.

2. EXPERIMENTAL

2.1. Sampling

PM_{10} airborne particulate matter was collected at four sites in Shanghai (Figure 1). The first site is located at People's Square at the intersection of three major streets with heavy traffic, which is the center of Shanghai City. The second site is located at a big courtyard in a residential area of Putuo District, which nears a street with little traffic. The third site is located at the edge of a little frequented road in Baoshan District, which is steel industry zone of Shanghai. The fourth site is located in a forest in Shanghai Institute of Applied Physics (SINAP) to the northwest 30 km from Shanghai City, which is free of traffic and was considered as the background. Medium volume PM_{10} samplers were used for the sampling of PM_{10} particulate matter. PM_{10} particulate matter was collected on polytetrafluoroethylene (PTFE) filters (ϕ=90 mm, pore size: 0.45μm), which have low blank concentrations for determination of trace elements. The samplers were placed on rooftops at a height of approximately 15 m. Forty-six of PM_{10} samples were collected at People's Square from December 2003 to December 2005. Sixteen samples were simultaneously collected at People's Square, Putuo, Baoshan and SINAP from January 2005 to March 2006.

Figure 1. Map of sampling sites in Shanghai:
A-People's Square, **B**-Putuo, **C**-Baoshan, **D**-SINAP

2.2. Analysis

Digestion of the PM_{10} samples was done according the following procedure: quarter of PM_{10} filters was digested with 8ml of aqua regia (HCl/HNO_3, 3:1, v/v) in PTFE vessels by a microwave digestion system (Ethos-320 Milestone) using a controlled program with stepwise increase of power, temperature, and maximum pressure to 900 W, 190 ^{o}C, and 300 psi, respectively. The vessels were cooled, 2 ml of HF was added and they were placed again in the microwave oven for 30 min at 900 W. The resulting solution was transferred into a PTFE beaker and heated to dryness. 2 ml of HCl was added and heated to dryness. The last step was repeated at twice to ensure elimination of total HF. The samples were finally diluted to 10 ml with 1 M HCl and stored in HDPE container. Blank solutions were also prepared with

unexposed filters in parallel. To avoid Pt contamination, the PTFE vessels were cleaned with 5 ml of HNO_3, placed in the microwave oven and finally rinsed with deionized water (> 18 MΩ, produced by Millipore Milli-Q purifier) before use.

Pt was determined by ICP-MS (X-7 Model, Thermo Elemental, England). The operating conditions used in the ICP-MS determination are summarized in Table 1. The sensitivity and stability of the instrument were tested with 1 ng ml^{-1} tune solution every operation by performing a short-term stability test. The influence of the main spectral interference on Pt determination in the airborne particulate matter by ICP-MS is HfO^+ on ^{195}Pt. The interference can be corrected mathematically by estimating the contribution of interfering element Hf to Pt signals in Hf standard solutions (Gomez *et al.*, 2000). Following equation was used for the correction:

$$I_{Pt} = I_{Pt,S} - (I_{Hf,S} \times R_{HfO,Hf})$$

where I_{Pt} is the corrected Pt intensity, $I_{Pt,S}$ is the apparent Pt intensity in the sample, $I_{Hf,S}$ is the Hf intensity in the sample, $R_{HfO,Hf}$ is the ratio of HfO^+/Hf^+ determined previously in Hf standard solutions. In this work, $R_{HfO,Hf}$ was obtained by determination 1 μg l^{-1}, 5 μg l^{-1}, and 10 μg l^{-1} Hf standard solutions.

Table 1. ICP-MS instrumental operating conditions

Nebulizer	*Micro concentric*	Scanning mode	*Peak jumping*
Sampling cone	*Nickel*	Resolution	*Standard*
Spray chamber temperature	*3 °C*	Dwell time	*10.0 ms*
Nebulizer gas flow	*0.85 l min^{-1}*	Sweeps	*1500*
Auxiliary gas flow	*0.85 l min^{-1}*	Acquisition time	*99 s*
Cool gas flow	*13.5 l min^{-1}*	Sample uptake rate	*0.8 ml min^{-1}*
RF power	*1150 w*	Runs/Replicates	*3*

The PGE certified reference materials, BCR-723 (Zischka *et al.*, 2002) (Road dust, issued by IRMM, European Commission) and GPt-3 (Yan *et al.*, 1998) (Peridotite, issued by IGGE, China), were analyzed in this study to evaluate the analytical quality. The results are shown in Table 2. Analytical results of Pt for BCR-723 and GPt-3 are in good agreement with certified values, which are within 1σ error of the certified values. The comparable results with the certified value for BCR-723 and GPt-3 indicate that the results of this work are reliable.

Table 2. Measured and certified Pt concentrations in BCR-723 and GPt-3

Certified reference material	Repetitions	Present results (ng g^{-1})	Certified value (ng g^{-1})
GPt-3	7	6.0±1.4	6.4±0.9
BCR-723	10	78.2±5.9	81.3±3.3 [10]

3. RESULTS AND DISCUSSION

3.1 The annual trends of the Pt concentrations in Shanghai air

Platinum concentrations in forty-six PM_{10} samples collected at People's Square of Shanghai from Dec. 2003 to Dec. 2005 are shown in Figure 2. The highest Pt concentration was 4.64 pg m^{-3}, while the lowest value was 0.43 pg m^{-3}. The average value of the Pt concentrations in these PM_{10} samples was 1.69±0.93 pg m^{-3}. Although there was some fluctuation, the increase of the Pt concentrations was not significant over the two years. Zereini *et al*. (2001) studied Pt concentrations in airborne particles in Offenbach and Frankfurt, Germany from 1988 to 1998. They have found that the Pt concentrations in the air have increased from an average of 3 pg m^{-3} in 1988 to 147 pg m^{-3} in 1998. There was about 46-fold increase in the Pt concentrations over a 10-year period. The increase of Pt concentrations in Shanghai air was not significant, possibly due to the shorter monitoring time. Since the number of cars equipped with three-way catalytic converters is increasing in Shanghai, the Pt concentration in Shanghai air should be

monitored over the next few years.

3.2 Seasonal variation of the Pt concentrations in Shanghai air

The Figure 3 shows average Pt concentrations in Shanghai air from January to December of 2004 and 2005, respectively. Seasonal variation of the Pt concentrations was significant. The Pt concentrations were lower from May to September (i.e., in summer and autumn) of 2004 and 2005, and the fluctuation of the Pt concentrations was smaller over the period. The Pt concentrations have higher values on January, March and November (i.e., in winter and spring), respectively. The seasonal distribution of the Pt concentration in 2004 has similar pattern with that of 2005. Because of same sampling site and techniques for each sampling, it is assumed that the seasonal variations of Pt concentrations over two years are possibly due to meteorological influences (i.e., wind and rain).

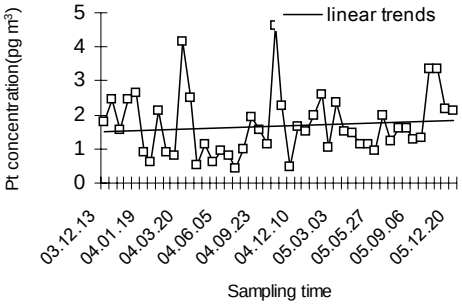

Figure 2. Pt concentrations in ambient air of the center of Shanghai from Dec. 2003 to Dec. 2005

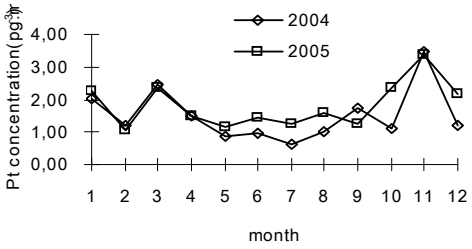

Figure 3. Average Pt concentrations in each month from 2004 to 2005 in Shanghai air

3.3 Pt concentrations at different sites in Shanghai

As described in the paragraph of sampling, sixteen of PM_{10} samples were simultaneously collected at four sites with different traffic intensity (i.e., People's Square, Putuo, Baoshan and SINAP) from January 2005 to March 2006. Average Pt concentrations were 2.58 pg m^{-3}, 1.27 pg m^{-3}, 0.75 pg m^{-3} and 0.54 pg m^{-3} at the People's Square site, Putuo site, Baoshan site and SINAP site, respectively (Figure 4). The People's Square site with heavy traffic had the highest Pt concentration, whereas the SINAP site that is free of traffic had the lowest Pt concentration. The Putuo and Baoshan sites with little traffic had medium Pt concentrations. The differences in the Pt concentrations at the four sampling sites suggest that the auto exhaust is the main emission source of Pt in Shanghai air. The Pt concentration at the SINAP site can be considered as the background value in Shanghai air. The Pt concentration at the People's Square site was higher 4-fold than the background value, which indicates that the Pt contamination is significant in the ambient air of the center of Shanghai. Rauch *et al.* (2005) have edited the data of Pt, Pd and Rh concentrations in urban air of some cities in Europe, the United States and Japan. Compared with those data, the Pt contamination level in Shanghai air is lower than one in urban air of some cities in Europe, the United States and Japan.

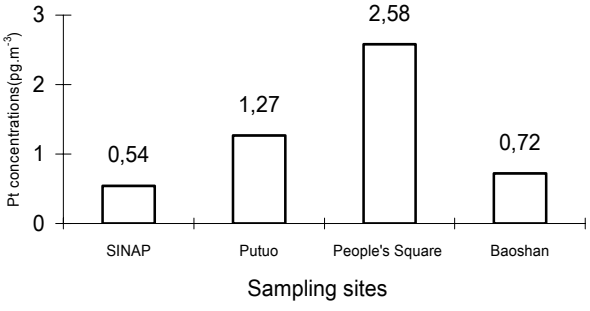

Figure 4. Pt concentrations in different traffic intensity in Shanghai

4. CONCLUSIONS

The average Pt concentration in the air of the center of Shanghai was 1.69±0.93 pg m^{-3}. The increment of Pt concentrations in Shanghai air was no significant from December 2003 to December 2005. The seasonal variations of Pt concentrations over two years are possibly due to meteorological influences. The analytical results of the sixteen samples simultaneously collected at four sampling sites with different traffic intensity in Shanghai show a clear dependence between Pt concentrations and traffic intensity, which suggest that the auto exhaust is the main emission source of Pt in Shanghai air. Compared with the Pt background value of 0.54±0.03 pg m^{-3}, the Pt contamination in the ambient air of the center of Shanghai is significant. However, the Pt contamination level in Shanghai air is lower than one in urban air of some cities in Europe, the United States and Japan. Since the number of cars equipped with three-way catalytic converters is increasing in Shanghai, the Pt concentration should be monitored over the next few years.

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