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Platinum group elements in the precipitation of the dry region of Xinjiang and factors affecting their deposition to land: the case of Changii City, China

Yuyan Liu [1], Fangfang Tian [1], Cheng Liu [1], Lan Zhang [2]

[1] *Department of Chemistry and Applied Chemistry, Changji University, Changji, Xinjiang, 831100, China*
[2] *The Analysis and Test Center, Capital Normal University, Beijing, 100048, China*

ABSTRACT

Platinum group elements and their compounds are a class of incident allergens and some platinum group element compounds also have carcinogenic effects. They accumulate in city environment as a result of emissions from catalysts used for vehicle exhausts. In this study, sixteen precipitation samples were collected on the north campus of Changji University located in the center of Changji. They were analyzed for palladium (Pd), platinum (Pt), and rhodium (Rh) by inductively coupled plasma–mass spectrometry. The average concentrations of Pd, Pt, and Rh were found to be 26.73 ng L^{-1} (range: 3.18–84.25 ng L^{-1}), 1.71 ng L^{-1} (range: below the detection limit to 6.38 ng L^{-1}), and 1.49 ng L^{-1} (range: below the detection limit to 3.53 ng L^{-1}), respectively. Pd deposition was most pronounced for single precipitation events, reaching 35.47 ng m^{-2} (range: 1.27–101.10 ng m^{-2}), followed by Rh (max. 4.96 ng m^{-2}, range: 0–14.85 ng m^{-2}) and Pt (max. 1.38 ng m^{-2}, range: 0–7.66 ng m^{-2}). Both Pd and Pt were higher in winter than in other seasons in terms of their wet deposition amounts and their concentrations in precipitation, whereas Rh was lower in winter. Moreover, the results indicated that discharge from coal combustion in winter, the amount of precipitation, and the number of dry days before rainfall events all significantly affected the wet deposition amount and precipitation concentration of platinum group elements. Pd deposition flux was highest (reaching 5.47×10^{3} ng m^{-2}) corresponding to 18 and 16 times the Rh and Pt fluxes, respectively. Finally, vehicle exhaust catalyst emissions from motor vehicles were not the only source of atmospheric platinum group metals in the city environment; in fact, combustion of coal in winter was found to be the dominant contributor of Pt and Pd in the atmosphere.

Keywords: *Platinum group elements, city environment, precipitation, wet deposition, influence mechanism*

Corresponding Author:
Yuyan Liu
☎ : *+86-994-2348148*
🖷 : *+86-994-2348148*
✉ : *liuyuyan006@126.com*

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1. Introduction

Platinum group elements (PGEs) and their compounds are a class of high–incidence allergens and some PGE compounds also have carcinogenic effects (Zereini et al., 1998; Kalavrouziotis and Koukoulakis, 2009; Orecchio and Amorello, 2011; Zereini et al., 2012; Mihaljevic et al., 2013). Palladium (Pd), platinum (Pt) and rhodium (Rh) are widely used in vehicle exhaust catalysts (VEC), in order to control vehicle exhaust and improve the air quality. Pt and Pd are involved in the oxidation of hydrocarbons and CO, while Rh is used in the reduction of nitrogen oxides (NO_X). Indirectly, they also result in a decrease of environmental lead pollution because these converters require the use of unleaded gasoline. The catalytic converters were first used in North America since 1970s, then used in Europe (early 1990s) (Barbante et al., 2001), and widely used after 2000 in China. This indeed resulted in a significant decrease of various chemical species in urban air pollution. However, they continue to be released into the environment after exhaust gas purification for particulate matter (Charlesworth et al., 2011; Orecchio and Amorello, 2011; Zereini et al., 2012; Mihaljevic et al., 2013). There has been much relevant research on PGEs (Zereini et al., 1998; Kalavrouziotis and Koukoulakis, 2009; Bonanno, 2011; Charlesworth et al., 2011; Mathur et al., 2011; Orecchio and Amorello, 2011; Zereini et al., 2012; Mihaljevic et al., 2013) and also a number of related domestic reports (Wang et al., 2007; Liu and Wang, 2011; Zhu et al., 2011; Li and Gao, 2012; Wang and Li, 2012; Pan et al., 2013), most of which were focused on the urban road environment with multi–media PGE temporal distribution factors, analysis of sources, analytical testing methods and other researches. PGE migration and transformation in the environment of arid regions have rarely been reported. Dry and wet deposition processes reduce the long–term accumulation of pollutants in the air, and they are important factors in maintaining a relatively stable atmospheric composition. Both dry and wet deposition of pollutants carry input to the surface and thus the terrestrial and aquatic ecosystems have been impacted (Grantz et al., 2003; Zhan et al., 2012). Due to a small amount of precipitation, wet deposition removes pollutants effectively, so the wet deposition of atmospheric pollutants has a profound significance (Grantz et al., 2003; Muezzinoglu and Cizmecioglu, 2006).

The city located in Xinjiang China which is in the center of Asia and Europe, and is known as the "Silk Road" of the new North Road. It has a typical continental arid climate, and the predominant wind direction is southwest. The annual precipitation is only about 200 mm. The heating period for the year is from October to April because of the cold winter, and coal has been the primary fuel used for heating. By the end of 2012, there were 140 000 vehicles in the city. As there is no large industry in the city, heating and vehicle emissions are the main sources of air pollution. Based on this information, in order to provide a reference for the in–depth study of urban environmental geochemical processes, we chose Changji in Xinjiang as a study area for the preliminary study of the wet deposition characteristics of PGEs in an arid urban atmosphere.

2. Materials and Methods

2.1. Sample collection

The selection of the sampling site was based on several factors, including ease of access, safety, minimizing potential for sample contamination, and representativeness. Sampling points were established on the Changji College North Campus. Based on the above criteria, the site chosen was Changji, which is located on the north slope of the Tianshan Mountains and the south margin of Junggar basin. It is at longitude 86°24'–87°37' and latitude 43°06'–45°20', which is in the center of Asia and Europe. Although the study area was in the downtown area of the city, it was more secluded and had less human interference than other areas in the city. The map of the study area is shown in Figure 1. The sampling period was one year (December 2011 through December 2012), and there were 87 precipitation events in total (40 rainy days, and 47 snowy days). Based on factors such as precipitation characteristics, six snowfall and ten rainfall events were selected for sampling (Table 1). The sampling container was polyethylene; it was washed with dilute nitric acid before precipitation to ensure that each sampling tool was free of pollution, and the container was secured while sampling. After the end of each precipitation, samples were frozen in polyethylene bottles at a temperature of –1 °C. A total of sixteen samples were collected.

***Figure1.** Map of the study area.*

2.2. Sample analysis

Main instruments and reagents. The main instruments and reagents used were as follows: TPC–3000 (Yankee Environmental System, YES), a home–built cyclone impactor, an Agilent ICP–MS 7500Ce inductively coupled plasma mass spectrometer, and a Milli–Q water purification system. The internal standard stock solution was prepared using the Re standard and the tuning solution was a thallium mixed standard solution preparation consisting of lithium, cobalt, yttrium, and cerium (Agilent, no. 5184–356).

Experimental methods. TPC–3000 (Yankee Environmental System, YES), and the home–built cyclone impactor were placed on a concrete platform with the sample intake at roughly 1 m above the surface. As soon as the precipitation sensor indicated the beginning of a precipitation event, the sampler was opened by an electric motor. The collection vessel was normally kept covered with a lid during periods of no precipitation. Samples were removed from the freezer and allowed to melt naturally at room temperature. Then the samples were analyzed directly after passing through the 0.45 µm membrane water. When we applied ICP–MS to determine the trace elements of Pt, Pd, and Rh in the samples, we found that Pt and Rh were interfered by small mass peaks. ^{108}Cd, ^{68}Zn, ^{40}Ar, ^{92}Mo, ^{16}O, ^{90}ZrO, ^{65}Cu, ^{40}Ar, ^{36}Ar, ^{69}Ga, ^{88}Sr, ^{17}O, and other interferences were generated on Pd, which could cause some difficulty when trace Pd is determined accurately. Therefore, in order to measure PGEs in samples accurately, Pt and Rh were determined using the normal mode while the ORS was used to measure Pd. ICP–MS conditions were optimized for the two selected modes before determination. The main operating parameters of the instrument were as follows: RF power 1 450 W, cooling gas 15.0 L min^{-1}, auxiliary gas 1.0 L min^{-1}, carrier gas 1.06 L min^{-1}. The isotopes of ^{103}Rh, ^{108}Pd, and ^{195}Pt were used for the analysis. The calibration standard solutions were prepared from a standard stock solution by dilution with 5% nitric acid. Detection limits of Rh, Pd, and Pt were 8.15×10^{-4}, 7.14×10^{-3}, and 6.71×10^{-3} ng g^{-1}, respectively. Their recoveries were more than 85%, and the relative standard deviation was less than 2.5%.

3. Results and Discussion

3.1. The PGE concentration in precipitation and influencing factors

PGE concentrations in precipitation. The average concentration in the precipitation of Pd was 26.73 (3.18–84.25) ng L^{-1}. In that range, the highest value occurred in the snowfall on January 17, 2012, and the lowest value occurred in the rainfall on June 3, 2012 and October 7, 2012. The average concentration of Pt was 1.71 (below detection limit, n.d.–6.38) ng L^{-1}, in which the highest value occurred in the snowfall on January 17, 2012 and Pt concentrations were below the detection limit in all rainfalls. The average concentration of Rh was 1.49 (n.d.–3.53 ng L^{-1}), in which the highest value appeared in the rainfall on April 29, 2012, and the lowest value appeared in the snowfall on December 31, 2011, February 6, 2012, and February 7, 2012, respectively. The Rh concentrations were all below the detection limit in these three snowfall events (Figure 2).

Seasonal variation of PGE concentrations. The seasonal variation trends of Pd and Pt concentrations are close to each other. They are higher in winter and lower in other seasons and they are higher in the snow and lower in the rain (Figure 2). The trend of Rh is the opposite of Pd and Pt, which is lower in winter and higher in other seasons, while it is lower in the snow and higher in the rain, except for sample 2–1 (Figure 2).

Influencing factors. Meteorological conditions are the main factors that influence the atmospheric pollution (Valiulis et al., 2002; Gunawardena et al., 2013). There were only long dry periods lasting 12 days before the snowfall in January 17, 2012, and a small amount of rainfall (only 1.2 mm). PGE accumulation reached a high level for a long dry period, and PGE concentrations reached a high level because of a small amount of precipitation. This may be the main reason for the highest concentration of Pd and Pt in the snow on January 17, 2012. There had been rainfalls on June 3, 2012 and October 7, 2012. Although the antecedent dry days were longer, the rainfalls were relatively larger, so they diluted the PGE concentrations. These are the main reasons why the concentration of Pd reached its lowest level in precipitation on June 3, 2012 and