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Spatial and temporal distribution of platinum group elements (PGEs) in roadside soils from Shanghai and Urumqi, China

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Abstract
Purpose The aims of this study are to elucidate the temporal trend, spatial distribution and the source of platinum group elements(PGEs) in roadside soil from Shanghai and Urumqi.
Materials and methods The roadside surface soils from different types of road were collected in both Shanghai and Urumqi. The spatial and temporal distributions of PGEs in roadside soils were determined by ICP-MS.
Results and discussion The average annual PGE concentrations from different types of roads in Shanghai occurred in the following order: highway > urban road, suggesting that total PGE concentrations were associated with driving speed. However, no significant difference in the concentrations of PGEs from different roads in Urumqi indicated that other factors also affected PGE distribution, such as driving conditions and traffic density. The temporal trends of PGEs were different between Shanghai and Urumqi. Levels of PGEs were low in spring and summer and high in autumn and winter in Shanghai. However, the trend was reverse in Urumqi because of the different forms of precipitation (rain vs. snow) and the occurrence of dry weather conditions in that city. Additionally, the highest concentration of Pt (23.5 ng g^{-1}) was observed in winter in Urumqi, suggesting that coal combustion may be another important source of Pt in northern Chinese cities.
Conclusions This study suggests that the spatiotemporal distribution of PGEs in soils is affected by the age of the catalytic converter used, traffic density, the type of catalytic converter used, and weather conditions. Although the PGEs were usually thought to be mainly from the abrasion and deterioration of catalytic converters, the coal combustion is also an important potential source of Pt, especially northern cities where coal combustion is high in winter.

Keywords Distribution · Platinum group elements · Precipitation · Roadside soil · Source analysis · Spatiotemporal

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1 Introduction

Most exhaust systems of gasoline-powered cars produced today are equipped with catalytic converters that contain platinum group elements (PGEs), such as palladium (Pd), platinum (Pt), and rhodium (Rh), to clean vehicle exhaust. Pt and Pd are involved in the oxidation of hydrocarbons and CO, while Rh is used in the reduction of NO_x. Indirectly, they also result in a decrease in environmental lead pollution because these converters require unleaded gasoline. Catalytic converters were first used in North America in the 1970s, have been used in Europe since the early 1990s (Barbante et al. 2001), and have been widely used since 2000 in China. Their use has led to a significant decrease in various chemical species in urban air pollution. However, it has been demonstrated that the concentrations of PGEs have increased significantly in the environment since their use in catalytic converters has been adopted. Many studies have suggested that the increase in PGEs in urban environments is mainly caused by the abrasion and

deterioration of catalytic converters, although there are other sources of PGEs in the environment (Ravindra et al. 2004; Pan et al. 2009). For example, Artelt et al. (1999) suggested that the emission rate of PGEs ranged from 2 to 120 ng km^{-1}, depending on different test conditions and the age of the catalytic converter. Consistently, the highest concentrations of PGEs are observed in the roadside soils/dusts from areas with high traffic density (Jarvis et al. 2001; Gomez et al. 2002; Djingova et al. 2003; Jackson et al. 2007), and the concentrations drop by over one order of magnitude within 10 m of roads (Jarvis et al. 2001). There is presently a lack of data on the potential ecotoxicity and toxicity of PGEs, particularly for Pd and Rh, so there is the potential that increasing quantities of PGEs may pose risks to human health. Numerous studies have investigated PGE accumulation in different environmental media near roads, such as road dust, airborne particles, soils, and organisms (Moldovan et al. 2001; Jackson et al. 2007; Colombo et al. 2008).

Since urban soils have highly variable properties, contain large numbers of foreign artefacts, and include different species of pollutions, urban soils attract a great deal of scientific attention (Baumgartl 1998). Metals and metalloids in urban soils have been studied because of their toxicity, persistence, and potential exposure via inhalation, ingestion, and dermal contact (Biasioli et al. 2006). Although particulate PGEs are thought to be less bioavailable in soils, they can be transformed into more reactive and mobile species. Therefore, it is important to investigate the long-term accumulation of PGEs resulting from the use of catalytic converters in vehicles (Lustig et al. 1996; Rauch and Morrison 1999; Moldovan et al. 2001). The distribution and behavior of PGEs in roadside soils have been investigated in many developed countries in Europe and North America (Schäfer and Puchelt 1998; Mihaljevič et al. 2013). However, less information on PGE abundance is available in China, where the government has implemented measures on new cars equipped with catalytic converters since the late 1990s. Pan et al. (2009) reported on the accumulation of PGEs in soils from some metropolitan cities, such as Beijing, Guangzhou, Shanghai, and Hong Kong. Most cities investigated previously are all in East China with heavy traffic and precipitation. There is lack of data about PGE pollution for cities in West China with relatively arid climates and less precipitation. Considering that PGEs in soils mainly originated from atmospheric deposition, the precipitation should be important for the PGEs transportation from atmosphere to the soils. Thus, the transportation of PGEs between humid and arid area should be different, resulting in a different seasonal change. However, few studies have been carried out to investigate the temporal distribution of PGEs in soils under different weather conditions.

The soils samples can reflect long-term accumulation of PGEs, and the PGEs may also transfer after they are deposited/absorbed in the soils, therefore, this study focuses on the seasonal change of PGEs not seasonal accumulation. The aims of this study are: (1) to investigate and compare the temporal and spatial distribution of PGEs in roadside soil from Shanghai and Urumqi; and (2) to analyze the potential sources of PGEs in the two cities.

2 Materials and methods

2.1 Study area

After considering the geophysical and economic conditions of various Chinese cities, we selected Shanghai and Urumqi as study sites for this investigation. Shanghai is located at the head of the Yangtze River delta in Eastern China, between longitudes 120°52′–121°45′E and latitudes 30°23′–31°27′ N (Fig. 1). Shanghai has a subtropical monsoon climate, with an annual temperature of 16 °C and average annual rainfall of 1200 mm. Shanghai is one of the most developed cities of China, and the number of motor vehicles exceeds 250 million, so the amount of PGEs emitted by vehicles is expected to be high. Urumqi lies west of the Bogda Mountains at the southeastern edge of Junggar Basin, between longitudes 86°37′E–88°58′E and latitudes 42°45′N–44°08′ N (Fig. 1). It has a temperate continental climate with an annual temperature of 6 °C and average annual rainfall of approximately 236 mm. Because of the rapid development of Urumqi, the number of motor vehicles has increased significantly from 100,000 to more than 500,000 in the past 10 years. The influence of the surrounding mountains in Urumqi would cause weak diffusion of airborne pollutants and therefore result in high deposition. Therefore, the PGEs are expected to be high in the atmosphere, despite the relatively low number of vehicles compared with Shanghai.

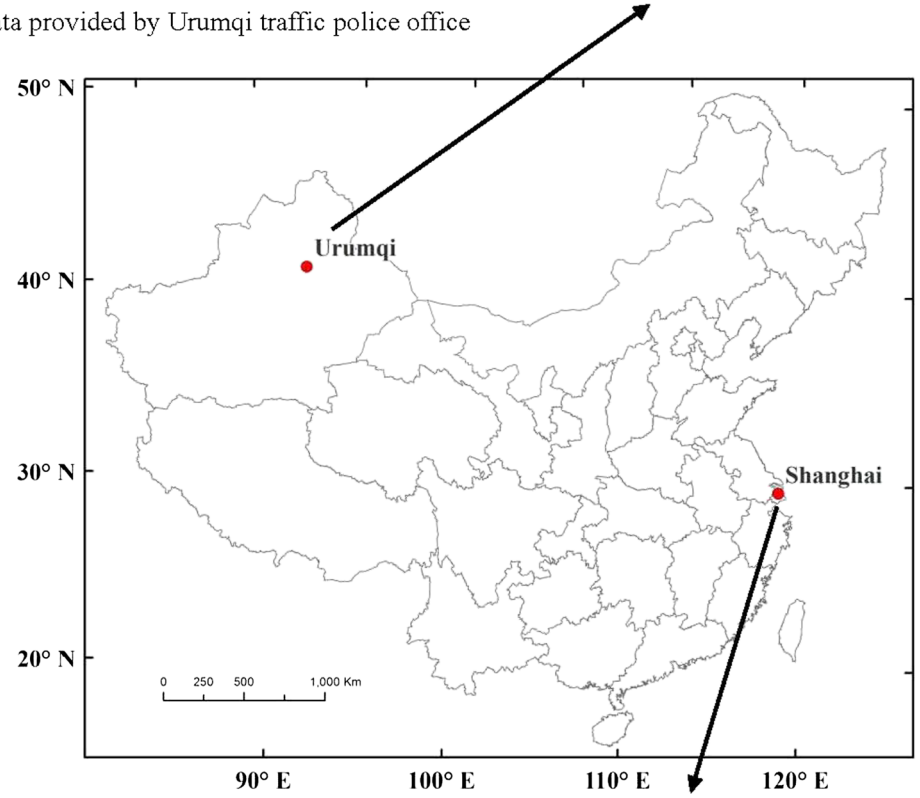
2.2 Sample collection

Different types of roads were selected from which to collect roadside soil samples. The urban road (Jinshajiang road: JSJ) and the highway that runs from Shanghai to Hangzhou (HH) were chosen as sampling sites in Shanghai. In Urumqi, the sampling sites were located on an urban expressway (Hetan road: HT), an urban main road (south of Youhao road: YH), an urban secondary road (South of Wenquan road: WQ), a suburban road (Qidaowan road: QDW), and a highway from Urumqi to Kuitun (UK). Considering the PGEs in the soil could be redistributed by even gentle winds, the soils were collected from both sides of the roads in Shanghai; sites were

Fig. 1 Sampling sites of roadside soils in Urumqi and Shanghai. Eight samples were collected from JSJ and HH in Shanghai, respective. Four sample were collected from HT, YH, WQ, UK and QDW in Urumqi, respectively. A total of 36 samples were collected in a year

city	site	abbrev	longitude	latitude	type	speed limit /km/h	traffic volume[a] /pcu/d
Urumqi	Hetan Road	HT	87°36′24″E	43°47′37″N	Urban road	80	6.21×10^4
	South of Youhao Road	YH	87°35′46″E	43°48′33″N	Urban road	50	3.86×10^4
	West of Wenquan Road	WQ	87°38′25″E	43°49′53″N	Urban road	60	1.81×10^4
	Urmqi-Kuitun Expressway	UK	87°17′19″E	43°56′33″N	Expressway	80	1.20×10^4
	West of Qidaowan Road	QDW	87°38′47″E	43°51′55″N	Suburban road	50	2.24×10^4

[a]Data provided by Urumqi traffic police office



city	site	abbrev	longitude	latitude	type	speed limit /km/h	traffic volume[b] /pcu/d
Shanghai	Jin shajiang road	JSJ	121°24′36″E	31°13′48″N	Urban road	50	2.08×10^4
	shanghai-hangzhou expressway	HH	121°22′48″E	31°7′12″N	Expressway	120	8.00×10^4

[a]Data provided by Shanghai municipal administration commission

designated as N-JSJ, S-JSJ, N-HH, and S-HH. However, results from Shanghai showed that the gentle wind had little impact on PGE distribution in soil, so soil samples were collected only on one side of the roads in Urumqi. In addition, the vehicles were thought to be driven at a relative constant speed when they were more than 200 m away from intersections. Considering the instability of PGEs emission caused by vehicle slowing and accelerating, a total of nine sampling points more than 200 m away from intersections were selected in this study. The details of the sampling locations were shown in Fig. 1.

Soil samples were collected in each season from the side of each road(less than 1 m from road side) when the surface of the soil had been dry for more than 3 days. The samples from Shanghai were collected in October 2007, January 2008, April 2008, and July 2008 and the samples from Urumqi were taken in October 2009, January 2010, April 2010, and July 2010. A total of 36 samples were collected; 16 samples from Shanghai and 20 samples from Urumqi. Surface soils (0–10 cm) were taken from the roadside using a polyethylene trowel prewashed with HNO_3 and stored in plastic bottles.

2.3 Sample preparation and analysis

The samples were dried at room temperature after twigs and stones were removed, then oven dried at 85 °C for 4 h until a constant weight was reached. The dried soils were gently ground and passed through a 75-μm stainless steel sieve. The procedure for the analysis of PGEs followed that of Liu and Wang (2011). In brief, 5.0 g of soils and 20 ml of aqua regia ($HCl:HNO_3$=3:1) were mixed in a 100-ml conical beaker. After being allowed to stand overnight, the mixture was digested at 120 °C on a hot plate until dryness was reached. The residue was then re-dissolved in another 20 ml of aqua regia, and dried again until 5 ml remained. About 1 mL of water was added to the residue, making the solution scattered. The solution was transferred after cooling, and diluted to a volume of 50 mL with ultrapure water. The final solution was shaken gently and left to stand for 2–3 days. A known amount of PGEs standard (0.5~10 times than PGEs in the samples) were spiked into soils, and the soils were conducted followed above procedure to obtain the method recovery. ^{103}Rh, ^{105}Pd, and ^{195}Pt were analyzed by ICP-MS after the solution was diluted by a factor of 50 with ultrapure water. Under optimal conditions, the detection limits for Rh, Pd, and Pt were 0.45 ng g^{-1}, 0.55 ng g^{-1}, and 0.47 ng g^{-1}, respectively. The duplicates were not conducted because the soils samples were completely mixed before analysis to avoid the heterogeneous of soils and the average method recovery was above 85 %. Moreover, the relative standard deviation of method recoveries was less than 2.5 %. Thus, the results are convinced and representative. The significance of difference among sites or seasons was analyzed. The difference between sites was analyzed by the data from each site (four seasons). And the difference between seasons was analyzed by the data from each season (all sites).

3 Results

3.1 Spatial and temporal distribution of PGEs in Shanghai

Average concentrations of PGEs were significantly different between seasons(p<0.05, T-test): they were higher in autumn (89.4±62.7 ng g^{-1}) and winter (118.2±109.2 ng g^{-1}), and lower in spring (18.3±14.1 ng g^{-1}) and summer (18.0±11.6 ng g^{-1}). Although PGE concentrations at all stations were higher in autumn and winter, the amplitude of variation varied between sampling locations, resulting huge standard errors. For example, PGE concentrations in autumn and winter from urban road (JSJ) soils (35.9±11.6 ng g^{-1} and 23.8±3.2 ng g^{-1}, respectively) were 2–4 times higher than those in spring and summer(12.4±0.4 ng g^{-1} and 11.3±0.9 ng g^{-1}, respectively); however, PGE concentrations in autumn and winter from highway (HH) soils (142.9±14.0 ng g^{-1} and 212.6±10.3 ng g^{-1}, respectively) were 6–8 times higher than those in spring and summer (24.2±21.3 ng g^{-1} and 24.7±14.7 ng g^{-1}, respectively) (Fig. 2a). PGE concentrations also varied between locations in the same sampling period. For example, PGE concentrations in HH (highway) soils were more than three times those in JSJ (urban road) soils collected in autumn. Generally, PGE concentrations in highway soils (average 101.1±86.9 ng g^{-1}) were much higher than those in urban road soils (average 20.9±11.6 ng g^{-1}) in a year (Fig. 2a) (p<0.05, T-test), indicating that catalytic converters in automobiles operated at high speeds would release more PGEs than those at low speeds (Ravindra et al. 2004). No significant difference was observed in PGE concentrations between two sides of the road. In terms of the PGE composition, the concentrations of Pd were significant higher than both Pt and Rh (p<0.05, T-test). Further, the temporal trend of concentrations of each element was similar to that of total PGEs, which occurred as follows: winter and autumn>spring and summer (p<0.01, T-test) (Fig. 3).

3.2 Spatial and temporal distribution of PGEs in Urumqi

Average annual PGE concentrations varied between locations, with the highest values occurring at YH (urban road, average 94.6±49.4 ng g^{-1}), and the lowest at QDW (suburban road, 28.6±7.3 ng g^{-1}, Fig. 2b). Average annual PGE concentrations in soils from different roads were not correlated with speed limit, This is not consistent with previous studies as well as our results in Shanghai (Hill and Mayer 1977; Artelt et al. 1999). For example, the roadside soil from YH, on which the speed limit is lower than the highway, contained the significant higher concentration of PGEs than other roadside soils

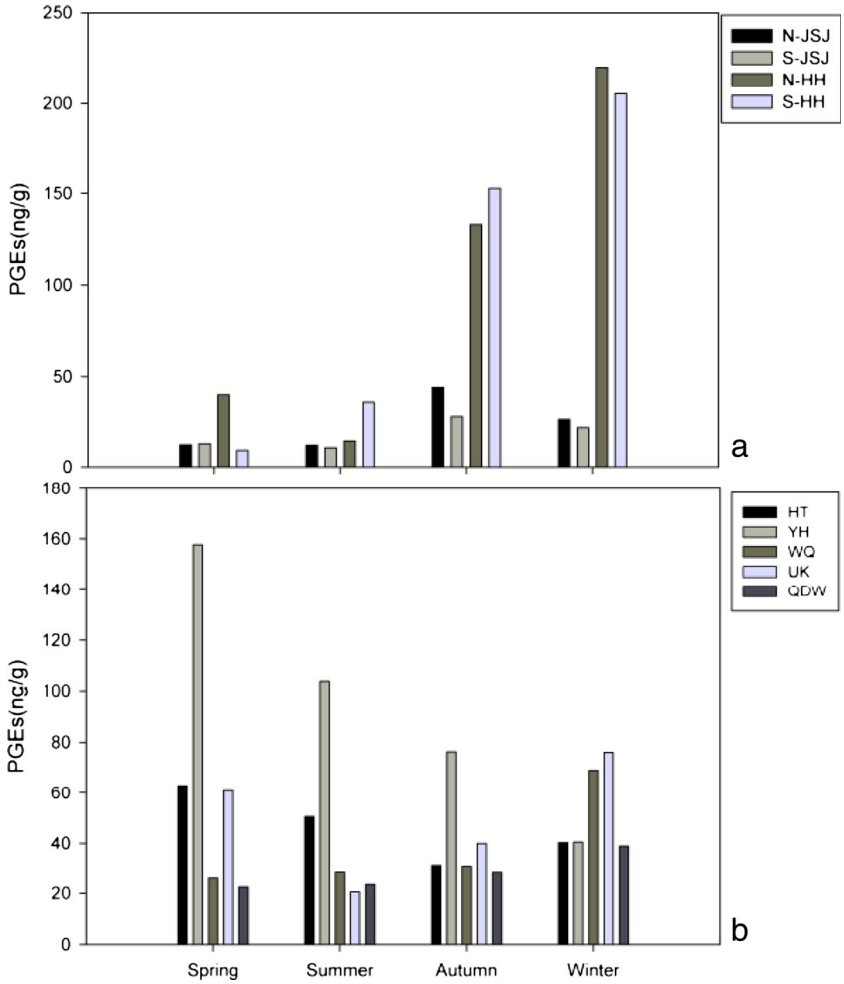


Fig. 2 Spatiotemporal distribution of total PGEs in Shanghai (**a**) and Urumqi (**b**). N- stands for north side of road, S- stands for south side of road

($p<0.05$, T-test). No consistent temporal trend was observed at any of the stations (Fig. 2b). For example, the PGE concentration decreased from spring (157.6 ng g^{-1}) to winter (40.5 ng g^{-1}) at YH (urban road), while the opposite trend was observed at WQ (another urban road), at which the peak PGE concentration occurred in winter (69.0 ng g^{-1}). In terms of the PGE composition, the concentrations of Pd were significant higher than both Pt and Rh ($p<0.05$, T-test) as same as Shanghai. Besides, lower concentrations of Rh and Pd generally occurred in winter, while the Pt concentration was significantly higher in spring and winter($p<0.05$, T-test), which indicates that Pt was the major factor contributing to the higher concentration of total PGEs in winter roadside soils from Urumqi (Fig. 4).

4 Discussion

4.1 Comparison of PGE concentrations and distributions

The concentrations of PGEs in these two cities were both much higher than the concentrations present in the continental crust (Pd: 0.4 ng g^{-1}; Rh: 0.06 ng g^{-1}; Pt: 0.4 ng g^{-1}; Wedepohl 1995). The highest concentrations of each element in both Shanghai and Urumqi were two orders of magnitude higher than the geogenic background values for Rh, and dozens of times higher for Pd and Pt. Between these two cities, higher average annual concentrations of PGEs in soils were expected to observe in Shanghai, because vehicles in Shanghai have been equipped with catalytic converters for longer periods of time and traffic flow in Shanghai is also much larger (Pan et al. 2013). However, the results showed no significant difference in concentrations of PGEs between Shanghai and Urumqi, indicating some factors affecting the concentrations of PGEs in soils.

The amount of PGEs emission from catalytic converters determined the PGEs accumulation in soils. Some factors were impact on the PGEs emission. For example, PGE concentrations in soils from highways (120 km h^{-1} speed limit) were much higher than those in soils from urban roads (80 km h^{-1} speed limit) ($p<0.05$, T-test) (Fig. 2a) in Shanghai, suggesting high driving speeds result in greater emissions of PGEs from catalytic converters (Ravindra et al. 2004). Consistently, PGE concentrations in highway soils from Urumqi

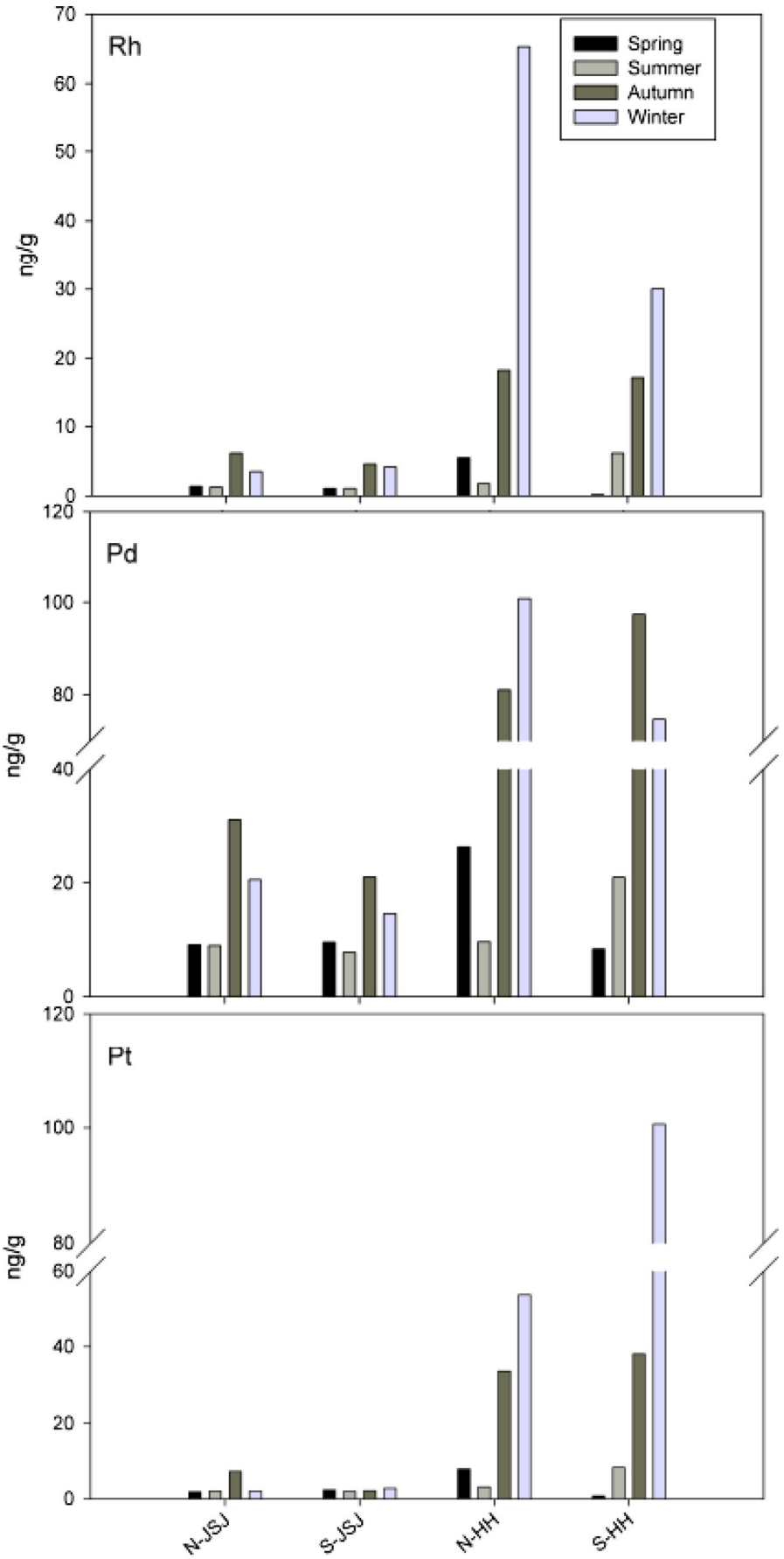


Fig. 3 Spatiotemporal distribution of Rh, Pd, and Pt in Shanghai

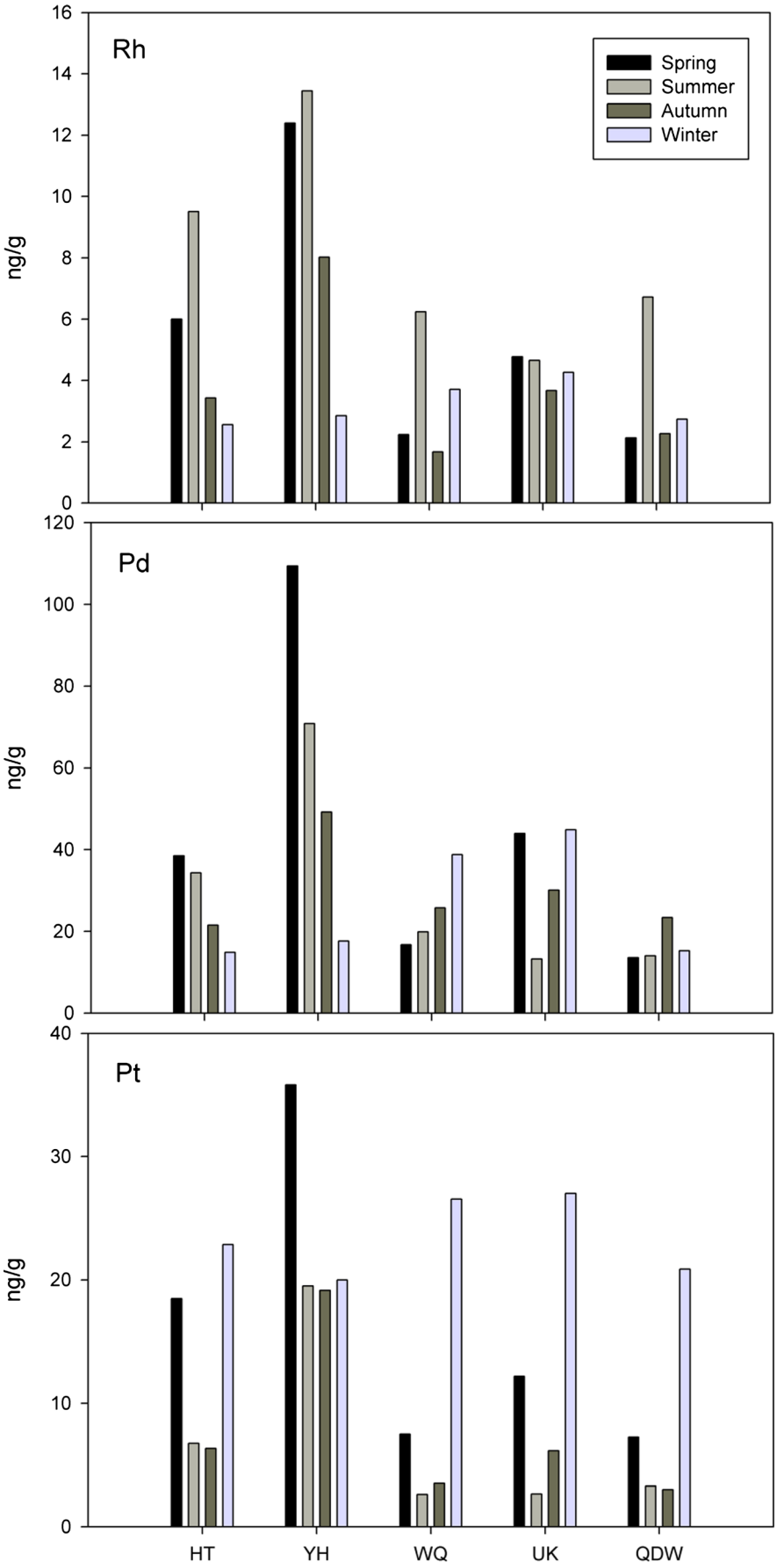


Fig. 4 Spatiotemporal distribution of Rh, Pd, and Pt in Urumqi

were lower than those from highway soils in Shanghai ($p<0.05$, T-test) because of lower driving speeds in Urumqi. However, there was no similar trend observed for urban road and highway soils in Urumqi. For example, PGE concentrations in soils from YH were higher than those at other roads, although the driving speed is lower at YH. This suggests that other factors also affect PGE emissions. For example, the PGE emissions from automotive catalytic converters under real-life driving conditions are higher than at constant speeds (Cubelic et al. 1997; Helmers 1997; Zereini et al. 1997; Ravindra et al. 2004). Additionally, Morton et al. (2001) suggested that PGE concentrations in soil are strongly dependent on traffic conditions; PGEs are released in greater quantities under high traffic densities than low traffic densities. Although the average speed on YH is lower than that on other roads, the traffic density of YH is much higher. Additionally, vehicles on YH may not be operated at a constant speed, unlike vehicles on highways, because of high traffic. Therefore, driving conditions and traffic density may also affect emissions of PGEs from catalytic converters.

Besides amount of emission from catalytic converters, the transportation of PGEs also play an important role in the concentration in soils. The PGEs may transfer from soils to other mediums, such as plants and water, resulting decreased PGEs concentrations in soils (Gomez et al. 2002). For example, the plant roots could absorb PGEs from soil. And surface runoff formed by rainfall might remove the accumulated PGEs in soils to water. However, these transportations might occur much less in Urumqi than Shanghai because of less water as medium in a result of arid weather.

In terms of the temporal distribution of PGEs, a significant difference was observed in Shanghai, with higher PGE concentrations in autumn and winter, and lower concentrations in spring and summer (Fig. 3). However, in Urumqi, higher PGE concentrations were observed in spring, and extremely high Pt concentrations were observed in winter (Fig. 4). Considering that traffic flow and the average speed of vehicles on roads change little throughout the year, the observed temporal trend may be caused either by the transport of PGEs, or different sources of PGEs in these two cities. The PGEs released from catalytic converters, which were reported to be a major source of PGEs, were divided into soluble-phase PGEs (accounting for less than 10 %) and particle-phase PGEs (accounting for more than 90 %) (Moldovan et al. 2002). In general, PGEs are immobile in water in vertical soil cores because of their hydrophobicity; however, the impervious surfaces of urban roads, such as cement, would enhance the horizontal movement of PGEs with runoff after rainfall, especially for particulate PGEs. This means that particulate PGEs may be removed from soil, and flow into sewers with runoff, resulting in lower concentrations in soils under conditions of high precipitation. This is consistent with our results from Shanghai, where PGE concentrations increased as rainfall decreased (Fig. 5), but is in contrast to results from Urumqi, where the impact of precipitation on PGE concentrations was dependent on the form and amount of precipitation. The main form of precipitation in Urumqi in winter is snow, which not only absorbs PGEs but also leads to their storage in the snow pack instead of soils; additionally, the snow pack prevents atmospheric deposition of PGEs to the soil by covering the soil. Thus, the concentration of PGEs was low in winter, during which the precipitation was also low. On the other hand, the amount of rainfall in Shanghai is four times that in Urumqi, which means that there may not be sufficient rainfall

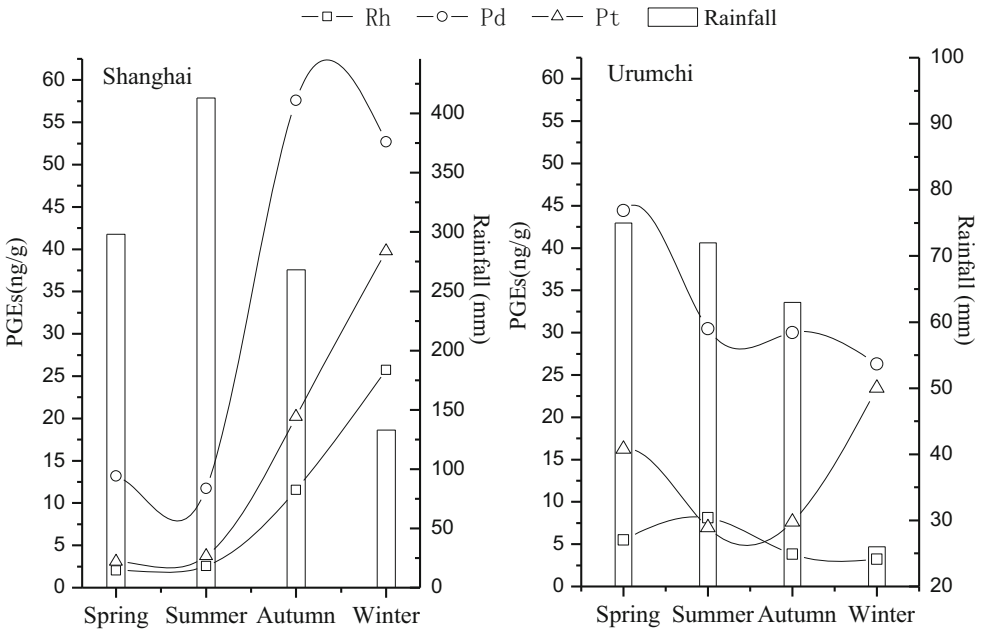


Fig. 5 The relationship between PGEs and precipitation

to create surface flow as in Shanghai; rainfall therefore does not remove PGEs from soils, but increases PGE concentrations in soils by washing PGEs from the atmosphere into soils. Additionally, when rising temperatures gradually melted snow above the surface soils in spring, the PGEs stored in the snow pack in the winter were released and preserved in surface soils because of their immobility, resulting in high PGE concentrations in soils in spring (Fig. 4). Many studies have shown peak concentrations of hydrophobic contaminants, such as PAHs, during snowmelt (Meyer et al. 2006). However, the peak Pt concentrations occurred in winter, which may be related to Pt sources, which will be discussed further in Section 4.2.

In comparison with foreign cities, concentrations of PGEs in surface soils from Chinese cities both in this and other studies are higher (Table 1). Because PGE concentrations in soils can reflect long-term accumulation of PGEs associated with the use of catalytic converters, many factors could contribute to this phenomenon, such as traffic conditions, and the age and type of catalytic converter used. For example, although catalytic converters were used in Macao as early as in developed countries, PGE concentrations in soils were lower as a result of lower traffic volume in that area (Pan et al. 2009). In Mumbai and Kolkata, the situation was different. Lower PGE concentrations in soils in these two cities may be because catalytic converters are not widely used in India; the Indian government has implemented Euro III emission standards for all new vehicles in 11 metro cities since 2005, and the number of new vehicles was only approximately 8 % of the total number of vehicles in operation in that country (Pan et al. 2009). Catalytic converters are continuously being developed. Vehicle exhaust catalysts have evolved from two-way catalysts containing Pt and Pd in the 1970s, to three-way catalysts containing Pt, Pd, and Rh in 1992, then to new three-way Pd-rich catalysts in the late 1990s (Ravindra et al. 2004). The installation of catalytic converters has been mandatory in China since 2000, which means most catalytic converters in vehicles in that country are of the newest generation, which are Pd-rich; it is therefore expected that higher levels of Pd will be observed in China. The order in which the concentrations of the three elements occurred (Pd>Pt>Rh) was the same in all Chinese cities. Gao et al. (2012) suggested that different Chinese cities may have similar types of catalytic converters. In foreign cities, the order in which the concentrations occurred was Pt>Pd>Rh (Table 1), indicating that the types of catalytic converters used were different than those used in China. Moldovan et al. (2002) suggested that different types of catalytic converters would release different amounts of PGEs, which may also result in different concentrations of PGEs between cities. Additionally, sample location, soil depth, and weather conditions (rainfall and wind) can also affect PGE concentrations in soil.

4.2 Source analysis of PGEs

Much higher concentrations of PGEs in soils than geogenic background values suggested that the contribution of anthropogenic sources to PGEs in roadside soils is significant in both Shanghai and Urumqi. Numbers of literature have demonstrated that the PGEs in roadside soils are from catalytic converters (Artelt et al. 1999; Tuit et al. 2000; Pan et al. 2009, 2013). For example, Morcelli et al. (2005) found a strong decrease of PGEs with increasing distance from traffic lane, which is as similar as other traffic-related elements (Zn and Cu). Therefore, the PGEs in roadside soils in Shanghai and Urumqi may be also from catalytic converters in vehicles. Concentrations of PGEs in soils not only reflect the accumulation of PGEs, but can also reflect the usage of catalytic converters in vehicles because catalytic converters are thought to be the major source of PGEs in cities. Ely et al. (2001) suggested ranges of ratios of 1–2.5 for Pt/Pd, 5–16 for Pt/Rh, and 4–9 for Pd/Rh; these are the ratios in which catalytic converters were estimated to emit PGEs.

Table 1 PGE concentrations (ng g^{-1}) in soils from different cities

City	Pt	Pd	Rh	Reference
Guangzhou	6.6–90.9	6.7–120.0	2.0–31.7	Pan et al. 2009
Mumbai	3.2–9.4	1.3–42.4	0.2–1.4	Pan et al. 2009
Kollcta	2.6–9.4	1.3–4.1	0.4–2.3	Pan et al. 2009
Macao	3.6–21.9	2.0–27.3	0.4–5.6	Pan et al. 2009
Hessen	2.0–159.0	1.0–7.0	1.0–28.0	Zereini et al. 1998
London	0.3–40.1	2.0–57.9	–	Farago et al. 1998
Naples	2.0–52.0	10.0–110.0	–	Cichella et al. 2003
Rome	7.0–19.4	–	–	Cinti et al. 2002
Nottingham 1982	0.3–1.4	0.6–1.0	–	Hutchinson et al. 2000
Nottingham 1996	0.2–1.3	0.2–1.1	–	Hutchinson et al. 2000
Shanghai	0.7–100.6	7.7–100.8	0.2–65.3	This study
Urumqi	2.6–35.8	13.2–109.4	1.7–13.5	This study

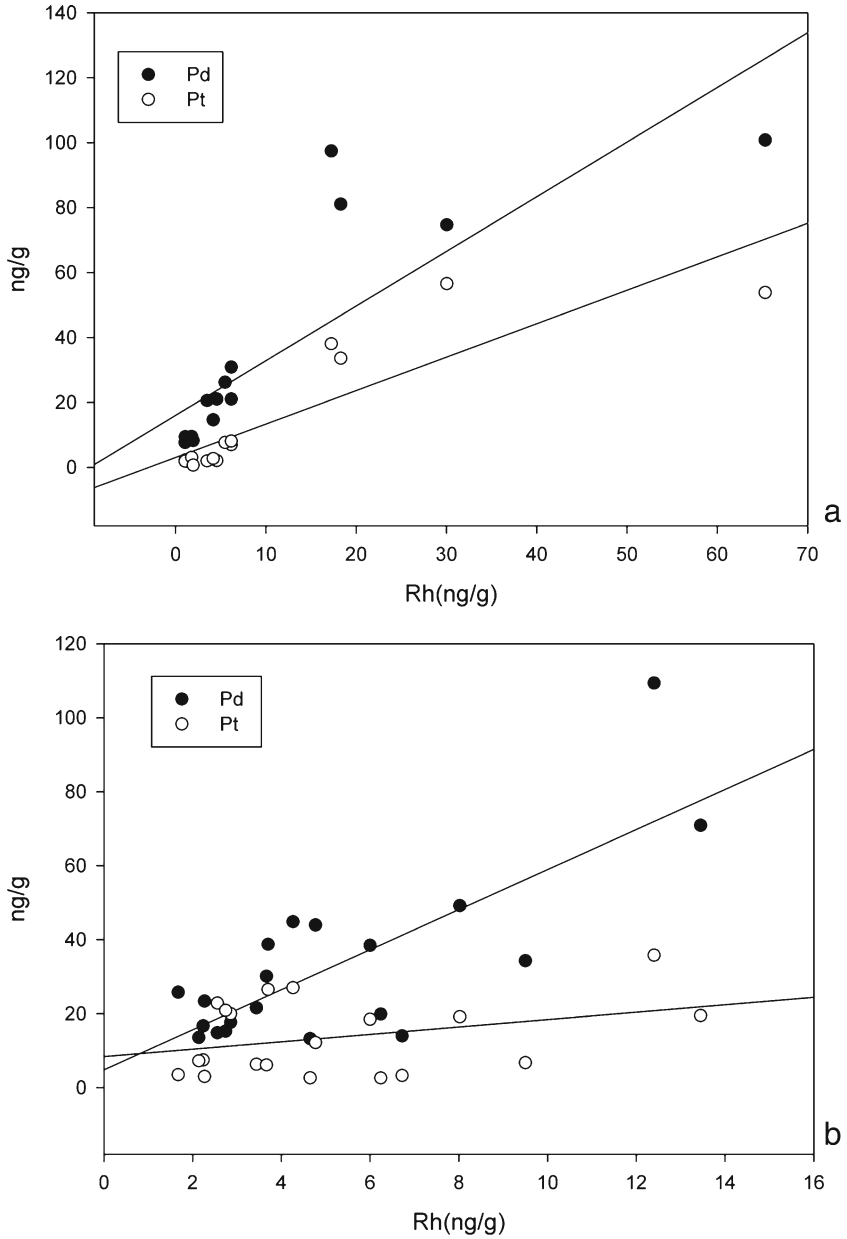


Fig. 6 The relationship between Rh and Pt (Pd) in Shanghai (**a**) and Urumqi (**b**)

However, our results indicated that the ratios in which PGEs were emitted from catalytic converters were wider ranging: 0.4–2.2 in Shanghai and 0.4–9.0 in Urumqi for Pt/Rh, 0.1–0.8 in Shanghai and 0.1–1.5 in Urumqi for Pt/Pd, and 1.5–8.8 in Shanghai and 2.1–15.4 in Urumqi for Pd/Rh. This can be explained by the different proportions of PGEs used in different generations of catalytic converters as discussed previously. Generally, the proportion of Rh was small and less varied, indicating that the amount of Rh required in catalytic converters required to remove nitrogen dioxide is consistent (Gomez et al. 2002). Conversely, the proportion of both Pt and Pd used in different types of catalytic converters is more variable, suggesting that Pt and Pd can be substituted for each other in catalytic converters. Thus, the ratio of Pt/Pd can be used to identify the type of catalytic converters. In both Shanghai and Urumqi, the ratios of Pt/Pd were below 1, except in winter in Urumqi, suggesting that Pd-rich catalytic converters are used in vehicles in these cities. Studies conducted between 1982 and 1996 in Nottingham, UK showed increased Pd and decreased ratios of Pt/Pd over that period, suggesting that Pd-rich catalytic converters are replacing the Pt-rich ones, even in developed countries (Table 1).

Since Rh was used for catalytic converters, approximately 73 % of the Rh production of the world had been consumed by the catalyst manufacturing industry until the end of the 1980s, which increased to 99 % until 2000(Ravindra et al. 2004). Thus, Rh was assumed to be derived mainly from catalytic converters, indicating positive correlations between Rh and Pt/Pd if catalytic converters were the only source of PGEs. Rh was significantly correlated with Pd and Pt in Shanghai

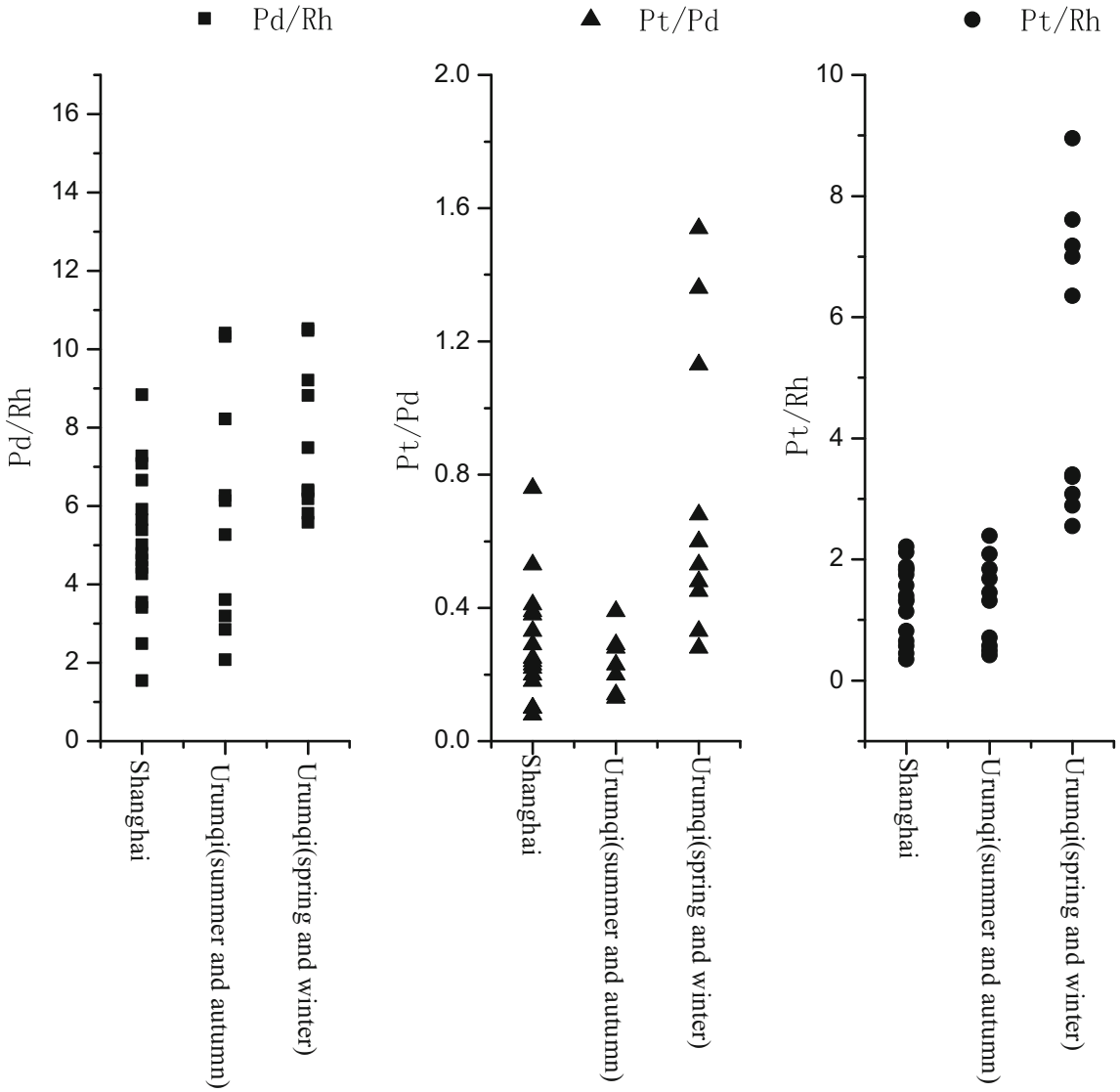


Fig. 7 Ratios of individual PGEs in Shanghai and Urumqi

(Fig. 6a) (R=0.83, p<0.01 for Pd and R=0.88, p<0.01 for Pt), suggesting that PGEs in soil from Shanghai mainly originated from catalytic converters. However, Rh was not correlated with Pt, suggesting a source other than catalytic converters of Pt in Urumqi in winter (Fig. 6b) (R=0.78, p<0.01 for Pd and R=0.34, p>0.1 for Pt). Moreover, the ratios of individual PGEs from summer and autumn in Urumqi were similar with those in Shanghai. However, the ratios from spring and winter in Urumqi were different from those in Shanghai. This further indicated a different source of PGEs in Urumqi in winter and spring (Fig. 7). Coal consumption is the primary source of energy in Urumqi for heating, coal power, and metallurgical industry (>70 %), especially during the winter when energy requirements are high. Previous studies have shown high amounts of Pd and Pt in coal, thus coal combustion is thought to be an additional source of PGEs in winter in Urumqi (Dai et al. 2003; Yang 2006; Qi and Gao 2008; Liu et al. 2014). However, the increase in Pd we observed in winter was not as high as that observed for Pt, which seems to contradict the notion that PGEs are derived from coal combustion. This may be explained by the bioavailability of PGEs; many studies have found that Pd is more bioavailable than Pt, which means that Pd is more easily transferred from soils to other mediums, such as water or plants, resulting in lower Pd in soils (Mihaljevič et al. 2013).

5 Conclusions

The spatial and temporal distributions of PGEs in roadside soils in Shanghai and Urumqi were investigated in this study. Mean concentrations of PGEs from different types of roads in Shanghai are in agreement with the previously observed trend that concentrations of PGEs are higher at roads with higher

speed limits. No such trend was found in Urumqi suggested traffic density and driving condition may also affect PGEs distribution. Compared with other cities, concentrations of PGEs in Shanghai and Urumqi were high. Unlike other cities, Pd in roadside soils from Shanghai and Urumqi was higher than other PGEs, indicating that Pd-rich catalytic converters were the main type of converters used in those two cities. The temporal distribution of PGEs varied between Shanghai and Urumqi as a result of differences in the amount and forms of precipitation and snowmelt. High Pt levels in winter in Urumqi indicate that coal combustion is another important source of PGEs in this city.

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