Dynamic change in particulate palladium concentrations in a mangrove wetland water environment and its mechanism in Dongzhai Harbor, China

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ABSTRACT

Palladium (Pd), in platinum group elements (PGEs), is widely used as a catalyst in vehicle exhaust catalytic converters (VECs). The cumulative level of Pd in the environment is growing rapidly, and the potential threat to human health is increasing. In this paper, the mangrove wetland in Dongzhai Harbor, Hainan Province, China, was taken as the research area for the collection of water samples. The particulate Pd was determined by microwave digestion and inductively coupled plasma-mass spectrometry (ICP-MS). The particulate Pd showed a decreasing trend from the estuary to offshore. The land origin of Pd in the mangrove wetland was explained. The Pd concentrations in the suspended state were lower in the wet season than in the dry season. Tide had an obvious influence on particulate Pd. The concentrations of particulate Pd at spring tide were higher than those at neap tide. The concentrations of particulate Pd at ebb tide were higher than those at flood tide. The rainfall intensity also had a strong influence on the particulate Pd. The particulate Pd increased after moderate and light rain but decreased after heavy rain. The pH, redox potential (Eh), and Cl⁻/C₀ had little effect on particulate Pd in the water environment. This study is helpful for understanding the environmental geochemical characteristics of Pd in mangrove wetlands and provides a theoretical basis for the study of Pd in urban coastal mangrove environment.

Key words | influence mechanism, mangrove wetland, Pd, suspended particulate matter, water environment

HIGHLIGHTS

- Pd is a new type of pollutant.
- Mangrove wetlands are important reservoirs of pollutants.
- The suspended Pd showed a decreasing trend from the estuary to offshore.
- Tide had an obvious influence on suspended Pd.
- The rainfall intensity also had a strong influence on the suspended Pd.

INTRODUCTION

Platinum group elements (PGEs) are widely used as catalysts in vehicle exhaust catalytic converters (VECs) because of their good catalytic performance (Bozlaker et al. 2014; Leopold et al. 2017; Birke et al. 2018; Fu et al. 2018). PGEs and their compounds are a class of substances with high sensitivity, and some PGE compounds also have carcinogenic effects (Rentschler et al. 2018). Traditional research suggested that PGEs entering the environment in a single state would not migrate and have effects (Fu et al. 2018). However, an increasing number of studies have shown that PGEs can dissolve, migrate, transform and enter the food chain under certain physical and chemical conditions, posing a major threat to human health. The impervious layer, especially road surfaces, is the main area...
where PGEs are enriched (Zereini et al. 2016; Fu et al. 2018; Liu et al. 2018). In the case of heavy rainfall, PGEs are very easily scoured by rainfall runoff, flow into the surface water environment and finally flow into estuaries (Suoranta et al. 2016). Since the 1990s, it has been found that palladium (Pd) in PGEs is less expensive and less toxic than platinum (Pt) and rhodium (Rh), so it has become a substitute for these elements. With the rapid increase in motor vehicles in recent years, the demand for PGEs, especially Pd, has risen sharply. The environmental problems brought about by the accumulation of PGEs have become increasingly serious in various countries worldwide; for example, Germany. At present, there are few reports on Pd in the urban coastal environment.

Mangrove wetlands are important reservoirs of pollutants (Fontana et al. 2012; Chowdhury & Maiti 2016; Krauss et al. 2017). At the same time, the complex hydrological, physical and chemical conditions in the intertidal zone make it easy for the deposited pollutants to re-enter the ecosystem and then cause secondary pollution of the ecosystem, making mangrove wetlands potential sources of pollutants (Fontana et al. 2012; Zhang et al. 2017). Dry and wet deposition also interfere with the transport of pollutants in mangrove wetlands. The concentrations of most pollutants in mangrove surface sediments in the dry season are higher than those in the wet season (Feng et al. 2017). Mangrove wetland pollutants are also affected by the interaction between tide and runoff.

Suspended matter is among the important material components of water bodies and plays an important role as a transmission medium during the migration and transformation of pollutants in receiving waters. Due to the large specific surface area of suspended solids, their ability to adsorb heavy metals pollutants is strong, and the concentrations of pollutants in suspended particulates are generally higher than those of water and surface sediments (Zhu et al. 2005; Ma et al. 2015).

The distribution source, ecotoxicity, migration and transformation of Pd have been discussed at home and abroad (Sutherland et al. 2015; Sen et al. 2016), but related research on Pd in mangrove wetlands has rarely been reported. In view of this, the mangrove wetland in Dongzhai Harbor, Hainan Province, China, was selected as the study area, and the dynamic change in particulate Pd in the water environment and its mechanism were analyzed. This study is helpful for understanding the environmental geochemical characteristics of Pd in mangrove wetlands and provides a theoretical basis for the study of Pd in the urban coastal mangrove environment.

**MATERIALS AND METHODS**

**Overview of the research area**

The Dongzhai Harbor mangrove wetland is located in the northeast of Meilan District, Haikou city, Hainan Province (110°32’E to 110°37’E, 19°51’N to 20°01’N). The wetland stretches over 50 kilometers, covers an area of more than 4,000 hectares and is the first and largest mangrove reserve in China. Dongzhai Harbor is similar to a funnel, with the northern end connected to the Qiongzhou Strait, and has an irregular semidiurnal tide. The study area has a tropical monsoon climate. The average annual temperature is 23.8 °C (28.4 °C in July and 17.1 °C in January). The annual rainfall is 1,700 mm, more than 80% of which is concentrated in May-October, forming obvious dry and wet seasons. The highest seawater temperature is 32.6 °C, the lowest is 14.6 °C, the average is 24.5 °C. The Dongzhai Harbor mangrove wetland is located in the estuary area and receives water from a total of four rivers, namely, the Yangzhou River, Sanjiang River, Yanfeng East River and Yanfeng West River. River water often flows with a large amount of rainfall runoff into Dongzhai Harbor. The study area has a relatively large population density, a large amount of domestic sewage discharge, and a large number of vehicles. Wang and other authors have shown that heavy metals and other pollutants in Hainan Island mangrove wetlands are substantially enriched (Wang et al. 2014; Ji et al. 2016).

**Sample collection**

According to the land use function of the mangrove wetland and its surrounding environment and the density of mangroves (Table 1), three sampling points (SPs) were established from the estuary of the mangrove wetland to offshore, in the following order: sampling point 1 (SP1), sampling point 2 (SP2) and sampling point 3 (SP3) (Figure 1). Water samples were collected at these SPs as follows: from June 2018 to June 2019, in the dry season (November–April) and wet season (May–October), water samples were collected at neap-spring tide and flood-ebb tide (two times each), a total of 48 water samples. According to the rainfall intensity, water samples were collected before and after light rain (daily precipitation less than 10 mm), moderate rain (daily precipitation of 10.0–24.9 mm) and heavy rain (daily precipitation of 25–49.5 mm) (twice per rain intensity), a total of 36 water samples. Using a CS-500 hand-held water quality sampling pump and plastic water...
pipe, water samples were collected at half the depth of the water (Table 2). Sampling tools are strictly cleaned to minimize the probability of sampling contamination. During sampling, a GPS tool was used to accurately locate and record the tidal fluctuations, temperature and rainfall.

**Analysis and testing**

**Major instruments and equipment**

An Agilent 7500Ce inductively coupled plasma-mass spectrometry (ICP-MS) instrument (Agilent Technologies, Santa Clara, CA, USA), a CEM microwave digestion instrument (CEM Corporation, Charlotte, NC, USA), a Pall water purification system (Pall, Port Washington, NY, USA), a UV spectrophotometer (Agilent Cary 60), and a multiparameter analyzer (Hach HQ 40d, HACH, Loveland, CO, USA) were used.

A standard stock solution of Pd (1,000 μg/mL, China Iron & Steel Research Institute Group) and a mixed standard solution of Li, Co, Y, Ce, and Ti (each at 1 ng/mL, Agilent, part # 5184–3566) were diluted with 5% nitric acid to produce a standard solution series. Guaranteed reagent-grade chemicals and ultrapure water were used for all procedures.

**Analytical methods**

The collected water samples were first measured for pH and Eh using a multi-parameter analyzer (Hach HQ 40d), and chloride ion content was determined by a UV-visible
spectrophotometer (Agilent Cary 60). Then use a 0.45 µm microporous filter to filter the sample and dry it at a constant weight to obtain suspended particles. Each sample was filtered through a 0.45 µm microporous membrane to obtain suspended particulate matter. Sampling 0.1 g was digested by microwave digestion using a HNO₃–HCl–HF (superior purity) digestion method, and the particulate Pd was determined by ICP-MS. Ten blank samples were randomly selected for analysis. Accurate analytical determinations of Pd were considerably hampered by spectral interferences of ¹⁰⁸Cd, ⁶⁸Zn, ⁴⁰Ar, ⁹²Mo, ¹⁶O, ⁹⁰ZrO, ⁶⁵Cu, ⁴⁰Ar, ³⁶Ar, ⁶⁹Ga, ⁸⁸Sr, and ¹⁷O, especially the interference of Sr oxide. Therefore, to ensure that Pd were accurately analyzed. The interference of Sr oxide were eliminated in advance, and used ICP-Q-MS (in collision mode with He) to effective minimize or eliminate the interference of other elements. The optimum conditions of ICP-MS were selected before the determination. The main operating parameters of the instrument were as follows: RF power 1,550 W, cooling gas 15.0 L/min, auxiliary gas 1.0 L/min, carrier gas 1.06 L/min and He gas flow at 5.00 mL/min. The isotope selected for elemental determination was ¹⁰⁵Pd. For PGE quality assurance and quality control, BCR-723 (Institute for Reference Materials and Measurements) and a standard material for PGE geochemical compositional analysis (GBW07290, National Standard Substances Center) were measured. The recoveries were 83–125%, and the relative standard deviation for each metal was <5%. The samples were treated and put into the refrigerator at 4 °C for storage to be tested.

## RESULTS AND DISCUSSION

### Distribution of particulate Pd in the water environment

#### Spatial distribution

In the dry and wet seasons, the average concentrations of Pd in the suspended state at SP1, SP2 and SP3 were 151.28 (25.93–285.38) ng/g, 110.55 (26.69–269.81) ng/g, and 91.57 (39.27–304.69) ng/g, respectively. The concentrations of particulate Pd at SP1 were the highest, followed by those at SP2 and then those at SP3, showing a decreasing trend from the estuary to offshore (Figure 2). In the crust, the background value of Pd is 0.4 ng/g. The concentrations of particulate Pd in the mangrove wetland of Dongzhai Harbor is 3–4 orders of magnitude higher than the background value. Dongzhai Harbor is located in the estuary zone, and Pd tended to decrease from the estuary to offshore, which indicated the terrestrial input of particulate Pd in the mangrove wetland. The results of studies by Mrutu and others on pollutants in estuary areas were consistent with our results (Mrutu et al. 2015).

### Seasonal variation

In the dry season, the average concentrations of particulate Pd at SP1, SP2 and SP3 were 151.63 (45.12–252.83) ng/g, 119.40 (36.76–250.43) ng/g, and 110.95 (42.51–304.69) ng/g, respectively. In the wet season, the average concentrations were 150.92 (25.93–285.38) ng/g, 101.71 (26.69–269.81) ng/g, and 72.20 (39.27–119.23) ng/g, respectively. The concentrations of particulate Pd in the dry season were higher than those in the wet season (Figure 3). Dongzhai Harbor has a tropical monsoon climate with abundant rainfall, simultaneous rain and heat, and distinct dry and wet seasons. The wet season precipitation accounts for approximately 80% of the annual rainfall. The Pd in wet season rainfall runoff was diluted, thus reducing the Pd concentrations in the input source. In the wet season, the temperature, total biomass, and microbial metabolic rate are high, and Pd is prone to migration (Ali et al. 2016). In addition, the dry season is the peak tourism season in Hainan, the number of cars increases, and Pd emissions to the environment increase, resulting in an increase in Pd concentrations in local mangrove wetlands. The above phenomena may explain why the concentrations of...
Figure 2 | Spatial distribution of Pd.

Figure 3 | The seasonal variation in Pd.
particulate Pd in the mangrove wetland in Dongzhai Harbor were higher in the dry season than in the wet season.

Factors affecting the accumulation of particulate Pd

The influence of neap-spring tide

The average concentrations of particulate Pd at SP1, SP2 and SP3 at spring tide were 124.13 (25.93–252.83) ng/g, 119.56 (26.69–250.43) ng/g, and 100.11 (42.51–304.69) ng/g, respectively. At neap tide, the corresponding average concentrations were 114.95 (74.34–151.73) ng/g, 85.45 (36.76–174.78) ng/g, and 74.90 (39.65–122.44) ng/g. The concentrations of particulate Pd at spring tide were higher than those at neap tide at each SP (Figure 4).

Hydrodynamic conditions are among the key factors causing the suspension of surface sediments. The concentrations of suspended matter have a profound impact on the concentration of pollutants. Affected by the topography and branch waterways of the mangrove wetland estuary, the water flow rate was enhanced during the spring tidal period, the sediment were strongly disturbed, the surface particles of the sediment floated up. The particulate Pd in the sediment were released, resulting the particulate Pd in the water environment increased (Ai et al. 2018; Yona et al. 2018).

The influence of flood-ebb tide

The average concentrations of particulate Pd at SP1, SP2 and SP3 at ebb tide were 184.47 (50.26–252.83) ng/g, 121.7 (49.29–225.08) ng/g, and 88.11 (42.51–96.68) ng/g, respectively. At flow, the average concentrations were 41.61 (25.93–118.81) ng/g, 83.31 (26.69–250.43) ng/g, and 85.91 (39.65–304.69) ng/g, respectively. The concentrations of Pd at ebb tide at each SP were higher than those at rising tide. During ebb tide, the Pd concentrations in the suspended state at SP1 were the highest, followed by those at SP2 and then those at SP3. During rising tide, the Pd concentrations in the suspended state at SP1 were the lowest, followed by those at SP2 and then those at SP3, which was contrary to the distribution trend of Pd observed at ebb tide.

Some studies have found that the tidal current speed in the early stage of the tidal fluctuation is higher than that in the middle stage. There is a significant positive correlation

Figure 4 | The influence of tide on Pd.
between the concentrations of suspended matter and the velocity of flow in the water environment (Bi et al. 2006; Gong et al. 2017). The direction of the ebb tide current is from the estuary to offshore, and the effect of runoff is enhanced in the offshore direction. The flow rates at SP1, SP2, and SP3 successively decreased. In addition, Pd is enhanced by terrestrial input during ebb tide. The concentrations of Pd in the suspended state at the three SPs gradually decreased at the time of ebb tide. The direction of rising tide current is from the offshore to the estuary. The flow rates at SP1, SP2, and SP3 successively increased, and the intensity of disturbance in the bottom sediment increased successively. The release intensity of particulate Pd in the sediment gradually increased, eventually resulting in a gradually increasing trend of particulate Pd concentrations at the three sampling points. The concentrations of Pd at ebb tide at each SP were higher than those at rising tide. Acceleration of water flow at ebb tide enhanced bottom sediment floating and particulate Pd release in sediment. The flow direction and runoff direction was consistent during the ebb tide period, and the strong water flow exacerbated the input of terrestrial Pd. The above factors may have been the main reasons for the particulate Pd concentrations at ebb tide being higher than those at rising tide. (Bi et al. 2006; Yona et al. 2018).

Impact of rainfall intensity

The average concentrations of Pd in the suspended state at SP1, SP2 and SP3 before light rain were 89.86 (25.93–153.80) ng/g, 65.89 (26.69–105.08) ng/g, and 49.70 (42.51–56.90) ng/g, respectively. After light rain, the average concentrations were 94.28 (68.30–120.26) ng/g, 71.34 (49.29–93.38) ng/g, and 66.66 (51.18–82.14) ng/g, respectively. Before moderate rain, the average concentrations were 168.55 (151.73–185.38) ng/g, 150.46 (126.14–174.78) ng/g, and 68.34 (58.07–78.61) ng/g, respectively. After moderate rain, the average concentrations were 189.83 (162.88–216.79) ng/g, 161.91 (54.02–269.80) ng/g, and 115.18 (111.14–119.23) ng/g, respectively. Before heavy rain, the average concentrations were 147.16 (146.12–148.20) ng/g, 108.17 (64.28–152.06) ng/g, and 93.02 (79.47–106.57) ng/g, respectively. After heavy rain, the average concentrations were 142.33 (112.01–172.65) ng/g, 49.17 (41.66–56.67) ng/g, and 50.32 (59.27–61.37) ng/g, respectively. Therefore, the concentrations of Pd in the suspended state increased after moderate and light rain at each SP, whereas the concentrations of particulate Pd decreased after heavy rain (Figure 5).

The impervious layer, especially road surfaces, is the main area of Pd enrichment (Zereini et al. 2016; Fu et al. 2018; Liu et al. 2018). In the case of abundant precipitation, Pd is easily washed by rainfall runoff and merged into the surface water environment, from which it is further transported to the estuary area (Suoranta et al. 2016). When the rainfall intensity is low, Pd in the land impermeable layer, especially road surfaces, and other terrestrial Pd are transported to the estuary by runoff, which leads to an increase in the particulate Pd concentration in mangrove water after light rain. When the rainfall intensity is high, rainwater has an obvious dilution effect on the Pd in runoff. At the same time, rainfall runoff scours and dilutes estuary pollutants, resulting in a decrease in the particulate Pd concentration after heavy rain (Mahmoodabadi & Sajjadi 2016; Zhao & Hou 2018).

Impact of water quality parameters

pH, Eh, and Cl\textsuperscript{−} are important water quality parameters. The effects of pH, Eh and Cl\textsuperscript{−} on water pollutants have been studied extensively. However, relevant discussions of PGEs are rarely reported.

In this paper, the correlations between pH, Eh and Cl\textsuperscript{−} and particulate Pd in the mangrove wetland water environment were analyzed. The correlation coefficient between the concentration of particulate Pd and pH was −0.10594, showing a weak negative correlation (p < 0.05, Figure 6(a)). The correlation coefficient of particulate Pd with Eh was 0.11087, showing a weak positive correlation (p < 0.05, Figure 6(b)). The correlation coefficient of particulate Pd with Cl\textsuperscript{−} was −0.06725, showing a weak negative correlation (Figure 6(c), p < 0.01). The above analysis revealed no significant correlations between pH, Eh and Cl\textsuperscript{−} and particulate Pd and showed that these parameters had little effect on particulate Pd. The results of studies by Bi and others on heavy metals tended to be consistent with our results.

CONCLUSIONS

The temporal and spatial distributions of particulate Pd in the mangrove wetland of Dongzhai Harbor, Hainan Province, were clear. The particulate Pd showed a decreasing trend from the estuary to offshore. The land origin of Pd in the mangrove wetland was explained. Compared with the dry season, during the wet season, the concentrations of particulate Pd were generally lower, precipitation was
more abundant, and the Pd in rainfall runoff was diluted. In addition, the migration of Pd during the wet season in Hainan was also caused by high temperatures occurring at the same time.

Tide had an obvious influence on particulate Pd. The particulate Pd concentrations at spring tide were higher than those at neap tide. The concentrations of particulate Pd at ebb tide were higher than those at flood tide. The rainfall intensity also had a strong influence on particulate Pd. The concentrations of particulate Pd increased after moderate and light rain but decreased after heavy rain. The water quality parameters pH, Eh and Cl⁻ had little effect on particulate Pd. In summary, the particulate Pd in the water environment of the Hainan mangrove wetland was mainly affected by tide and rainfall. The effects of pH, Eh and Cl⁻ on the particulate Pd in the water environment were weak. This study provides a theoretical basis for the study of particulate Pd in the urban coastal environment. Pd has

Figure 5 | Effect of rainfall intensity on Pd.

Figure 6 | Correlations between pH, Eh, Cl⁻ and particulate Pd.
potential health threats to organisms, and it is meaningful to quantitatively determine the bioavailability or bioaccumulation of Pd. The concentration of Pd in the dissolved state is also of great interest.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Rentschler, G., Rodushkin, I., Cerna, M., Chen, C., Harari, F., Harari, R., Horvat, M., Hruba, F., Kasparova, K., Krskova, A., Krsnik, M., Laamech, J., Li, Y.-F., Löfmark, L.,


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