Variation in palladium and water quality parameters and their relationship in the urban water environment

Yuyan Liu, Fangfang Ding, Caiye Ji, Dan Wu, Lin Wang, Bo Fu, Haofeng Liu and Lan Zhang

ABSTRACT

Palladium (Pd) is widely used in vehicle exhaust catalysts (VECs) to reduce toxic emissions from motor vehicles. The study aimed to quantitatively determine Pd content and water quality parameters, to analyze the variation differences and to explore the effect of water quality parameters on Pd content in the urban water environment system (wet deposition–rainfall runoff–receiving water body–estuary) of the city of Haikou, Hainan Island, China. The method used in this study included microwave digestion under high pressure and temperature, analysis by inductively coupled plasma mass spectrometry, quality control of the experimental procedure and guaranteed recovery (85% −125%). The results showed that the dissolved Pd average content in the urban water environment system was the highest in rainfall runoff (4.93 ng/L), followed by that in the receiving water body (4.56 ng/L), and it was the lowest in wet deposition (0.1 ng/L). The suspended Pd average content was the highest in the estuary (2.83 ng/L), followed by that in rainfall runoff (1.26 ng/L), and it was the lowest in wet deposition (6×10^{-4} ng/L). The particle–water partition ratio of the estuary Pd was the highest (1.26), followed by that of Pd in rainfall runoff (0.26). The particle–water partition ratio of the wet deposition Pd was the lowest (6×10^{-3}). The dissolved Pd was correlated with the pH, Cl^-, and total suspended solids (TSS) (correlation coefficient = 0.52, −0.68, 0.39, $p < 0.05$; regression coefficient = 1.27, −1.39, 0.01). The suspended Pd was only correlated with Cl^- and TSS (correlation coefficient = −0.36, 0.76, $p < 0.05$; regression coefficient = −1.45, 0.01). Cl^- and TSS were the most closely related to Pd in the water environment system. Although individual factors such as pH, Cl^-, and TSS had certain migration and transformation effects on Pd in the wet deposition–rainfall runoff–receiving water body–estuary system, the probability of strong correlations was not high. In particular, Eh was not related to the dissolved nor suspended Pd content (correlation coefficient = 0.14, 0.13), which may be due to the synergistic effect of the multiple physical factors on Pd. This study was helpful to better understand the environmental behavior of Pd and provided important theoretical support for the prevention and protection against urban water environmental pollution.

Key words | change law, correlation, palladium, physical and chemical factors, urban water environment

Yuyan Liu
Fangfang Ding
Caiye Ji
Dan Wu
Lin Wang
Bo Fu
College of Geography and Environmental Science,
Hainan Normal University,
Haikou, Hainan, 571158,
China

Haofeng Liu
Changji Environmental Monitoring Station,
Changji, Xinjiang 831100,
China

Lan Zhang (corresponding author)
Analysis and Testing Center,
Capital Normal University,
Beijing 100048,
China
E-mail: *dff960125@163.com*

HIGHLIGHTS

- Platinum group elements are a new class of pollutants.
- Islands and coastal cities have formed in a 'wet deposition–rainfall runoff–receiving water body–estuary' water pollution chain.
- There were significant differences in the water quality parameters (pH, Eh, Cl^-, TSS) of wet deposition, rainfall runoff, receiving water bodies, and estuary.
- Cl^- and TSS were the most closely related to Pd in the water environment system.
- Eh was not related to the dissolved nor suspended Pd content, which may be due to the synergistic effect of the multiple physical factors on Pd.

doi: 10.2166/wst.2020.303

INTRODUCTION

The rapid urbanization process has resulted in a rapid increase in urban impervious layers (Ma *et al.* 2016), intensified the formation of rainfall runoff, changed the urban water cycle, and promoted the development of the wet deposition–rainfall runoff–receiving water body–estuary pollution chain and water environment system in coastal cities. Pollutants migrate along this pollution chain, causing the entire city water environment to face ecological risks (Huber *et al.* 2016).

Platinum group elements (PGEs) are not only strategic metals used in catalysts, fuel cells and electronics, and cancer therapy, but also a new class of pollutants that can cause allergies, asthma and even cancer (Sutherland *et al.* 2015; Birke *et al.* 2018). Due to their excellent catalytic performance, PGEs are widely used in vehicle exhaust catalysts (VECs). The urban vehicle flow is large and dense. During the operation of motor vehicles, particles containing PGEs are continuously emitted with exhaust gases, and a large number of these particles settle and accumulate on the surface of impermeable beds; in particular, PGE enrichment on road surfaces is especially prominent (Zereini *et al.* 2016; Fu *et al.* 2018). During wet deposition, the PGEs accumulated in the atmosphere and on road surfaces will be leached and washed away during wet deposition and rainfall runoff, respectively, and enter the wet deposition–rainfall runoff–receiving water body–estuary urban water environment system (Suoranta *et al.* 2016).

Dahlheimer *et al.*(2007) found that the pH, Eh, Cl^- and other parameters (NO_3^-, SO_4^{2-}, PO_4^{3-}, fluxes) directly or indirectly affected the migration and transformation of PGEs (Dahlheimer *et al.* 2007; Mashio *et al.* 2016; Zereini *et al.* 2016). The role of pH, Eh, and Cl^- in increasing or decreasing the bioavailability of PGEs cannot be ignored; for instance, the presence of chloride in lung fluids may lead to the formation of halogenated PGE complexes (Wiseman & Zereini 2009). The presence of siderophores can significantly increase the solubility of PGEs at various pH levels, particularly that of Pd (Zereini *et al.* 2016). However, there have been few related research studies and a lack of systematic research on the entire urban water environment system. Studies have mainly focused on independent components of the wet deposition–rainfall runoff–receiving water body–estuary system (Liu *et al.* 2015; Fu *et al.* 2018). Therefore, the research will pay more attention to the migration and transformation of pollution in the entire pollution chain.

PGEs include Pd, Pt, Rh and other elements. Studies have found that the bioavailability of PGEs followed the order of Pd > Rh > Pt. The accumulation rate and activity of Pd in water bodies were higher than those of the other PGEs (Wiseman & Zereini 2009; Zereini *et al.* 2016). Compared with Pt, the price of Pd was relatively low, so Pd was used in VECs in large amounts (Birke *et al.* 2018).

This paper selected Haikou, Hainan Province, China, as the research region and focused on its natural environmental characteristics. The aim of this study was to quantitatively determine Pd content and water quality parameters, to analyze the variation differences and to explore the effect of water quality parameters on Pd content in the urban water environment system (wet deposition–rainfall runoff–receiving water body–estuary). This study will be beneficial to a more quantitative understanding of the behavior of Pd in the water environment and will provide basic information support for coastal water environmental protection at the same time.

MATERIALS AND METHODS

Overview of the study area

Haikou is located in the northern part of Hainan Island (19°32′–20°05′N, 110°10′–110°41′E), and the built-up area covers 140.59 km^2. Haikou is not only the political, economic, technological, and cultural center of Hainan Province but also the largest transportation hub, with severe traffic congestion in the urban areas. The number of motor vehicles exceeds 8×10^5 and the average traffic volume reaches 5.65×10^3 vehicles per hour. The local government has adopted an automobile purchase restriction policy to control the number of vehicles in Haikou. Haikou has a typical tropical monsoon climate, with abundant rainfall (an average annual rainfall of 1,684 mm). Rainfall runoff is prominent and typical. In recent years, the Haikou ambient air quality has maintained a national leading level (air quality index, AQI < 100), but the surface water environmental quality in its urban areas was relatively poor (Xu *et al.* 2013). The migration and accumulation of pollutants through the wet deposition–rainfall runoff–receiving water body–estuary water environment system may be the main reason.

Sample collection

The Meishe River originates in the Yangshan area in the south of Haikou city, runs through the north and south of Haikou city, and merges with the Qiongzhou Strait at Xingang Pier in Haikou city. The Wuyuan River also originates in the Yangshan area in the south of Haikou city, flows through the built-up area of Haikou city, and merges with the Qiongzhou Strait in Changliu town. The Meishe River and Wuyuan River are both the main and relatively independent rainfall runoff-receiving water bodies in the built-up area of Haikou city.

According to the routine monitoring requirements of wet deposition (Technical Specifications for acid deposition monitoring, HJ/T 165-2004 2004-12-09 implemented), Hainan Normal University was selected as the wet deposition sampling site in the built-up area of Haikou. According to the land use function and the urban main road network, three rainfall runoff sampling sites were set up in the catchment areas of the Meishe River and Wuyuan River. They are Hainan Normal University (HS; cultural and educational residential area), the intersection of Longkun South Road and Hongchenghu Road (LN; traffic-intensive area), and Banqiao Road (BQ; commercial area). According to the principle of setting river- and estuary-monitoring sections, three monitoring sections were located in the urban center sections of the Meishe River (MS) and Wuyuan River (WY), while one monitoring section was located in each estuary. These locations were used as sample collection sites for the receiving water body and estuary (Figure 1).

Eight wet deposition events (Table 1) of different rainfall levels were selected during the wet (May–October) and dry (November–April) seasons, and wet deposition and rainfall runoff samples were collected at the corresponding sampling points. After rainfall runoff had completely entered the receiving water body, receiving water body and estuary water samples were collected by using the electric water quality sampler at the same depth of the monitoring section of each river and its estuary.

A total of eight wet deposition samples, 24 rainfall runoff samples, 48 receiving water samples, and 16 estuary water samples were collected. Rainfall characteristics, such as rainfall amount, precipitation intensity and previous clear days, were also recorded.

Analysis and measurement

Main instruments and equipment

An inductively coupled plasma mass spectrometer (Agilent 7500ce), a CEM-MARS 5 microwave digester (CEM, USA),

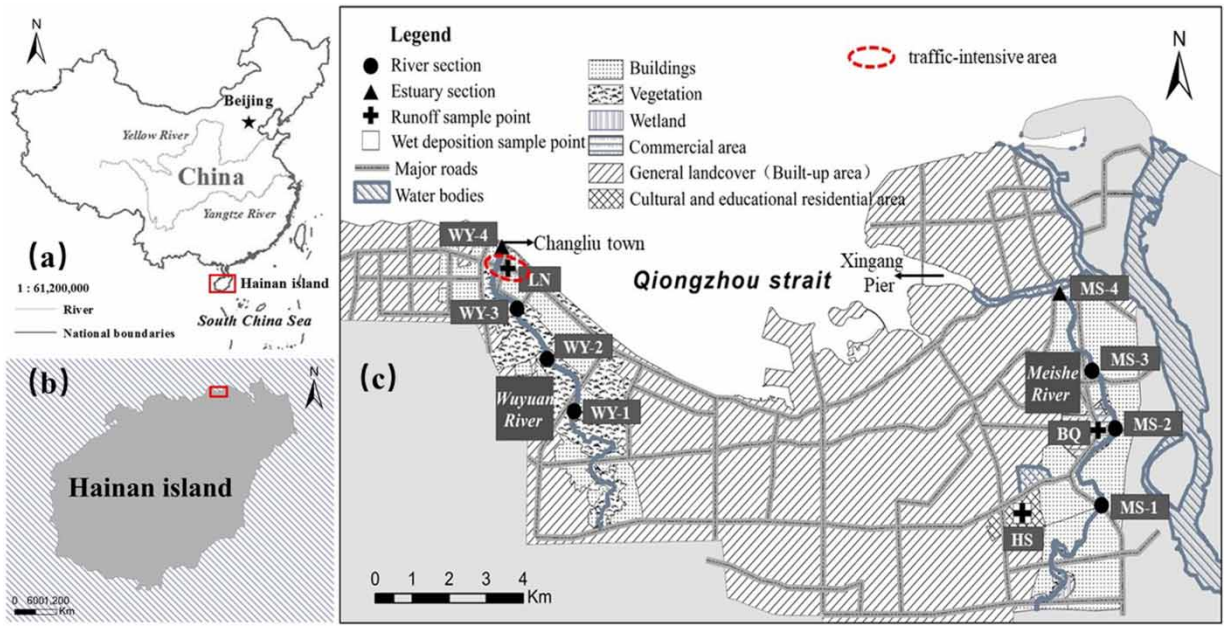

Figure 1 | Study area and sampling sites and the layout of the monitoring sections.

Table 1 | Precipitation parameters of each precipitation event

Date	2017/10/29	2017/11/17	2018/3/31	2018/4/12	2018/5/19	2018/6/15	2018/7/1	2018/10/15
Rainfall amount (mm)	7.8	16.4	25.6	29.5	15.3	66.1	47.8	34.1
Rainfall intensity (mm/min)	0.22	0.33	0.63	0.38	0.35	0.95	0.61	0.68
Clear days (day)	4	6	5	4	1	1	1	4

a UV-Vis spectrophotometer (Agilent Cary 60, Agilent Technologies, Santa Clara, CA, USA), and a multiparameter analyzer (Hach HQ 40d) were used.

Determination method

All samples were divided into two batches. One batch was used to measure the pH, Eh, and Cl^-. The other batch was filtered through a 0.45 μm microporous membrane to obtain the suspended matter content and filtered water samples, and the suspended matter and Pd contents were measured. The pH and Eh were measured using the multiparameter analyzer. The Cl^- content was determined with the UV-Vis spectrophotometer. The dissolved Pd in the filtered water samples was directly determined through inductively coupled plasma mass spectroscopy (ICP-MS). A 0.5 g sample was placed in a polytetrafluoroethylene digestion tank, and 6 mL HCl, 2 mL HNO_3, and 1 mL HF were added in sequence. Then digestion tank was placed in a fume hood for 40 minutes for pre-digestion. The digestion program was carried out by microwave digestion apparatus: the temperature was raised to 120 °C within 5 minutes and held for 5 minutes; the temperature was raised to 150 °C within 5 minutes and maintained for 5 minutes; the temperature was raised to 190 °C within 7 minutes and maintained for 40 minutes. The suspended Pd was determined via ICP-MS. Ten blank filter membrane samples were randomly selected. After weighing, the above method was used for digestion and determination, and the average value was taken as the blank of the element in the filter membrane. After processing, samples were put in a refrigerator and stored at 4 °C. The ICP-MS operating conditions were optimized before the measurements, and the standard mode was used. The isotope selected for the elemental measurements was ^{105}Pd. At the same time, the national standard materials GBW07290 and BCR723 were used to evaluate the recovery rate and reproducibility of the entire experimental process. The recovery rate of Pd is 92 ± 5%, and the reproducibility is better than 5%.

RESULTS AND DISCUSSION

Changes in the water quality parameters in the urban water environment system

The average pH values in wet deposition, rainfall runoff, receiving water bodies, and estuaries reached 6.23 (5.92–7.23, $n = 8$), 7.75 (7.22–8.35, $n = 24$), 8.23 (7.26–9.14, $n = 48$), and 8.13 (7.68–8.57, $n = 16$), respectively. The average pH decreased in the following order: receiving water body > estuary > rainfall runoff > wet deposition (Figure 2). Affected by the acidic pollutant gases (such as SO_2) emitted by motor vehicles, wet deposition has become the most acidic water body in the urban water environment system (Garaga *et al.* 2020). Due to incorporation of a large amount of construction pollutants (such as cements, bricks), urban impermeable layer sediments are generally alkaline. When runoff is formed during wet deposition and rainfall runoff continuously washes away urban impermeable layer sediments, the pH of runoff increases quickly (Liu *et al.* 2007). Receiving water bodies in coastal cities not only accept rainfall runoff with a higher pH but also cause notable seawater backflow when storm surges occur. The receiving water average pH is higher than that of rainfall runoff and wet deposition in inland cities (Zhou *et al.* 2017). The estuary not only receives water from cities in the middle and upper reaches but is also near the ocean, and the exchange between the estuary and ocean water is notable. The pH of the estuary increases due to the dual influences of the received water and seawater alkalinity, so the estuary water is also alkaline (Howland 2000).

The average Eh values in wet deposition, rainfall runoff, receiving water bodies, and estuaries reached 45.19 (−13.40 to 63.10, $n = 8$) mV, −42.38 (−70.99 to −12.68, $n = 24$) mV, −71.74 (−121.20 to −13.40, $n = 48$) mV, and −55.50 (−88.60 to −14.70, $n = 16$) mV, respectively. The average Eh decreased in the following order: wet deposition > rainfall runoff > estuary > receiving water body (Figure 2). The pH of the water body was significantly negatively correlated with Eh ($r = -0.97$, $p < 0.05$). The average Eh value in

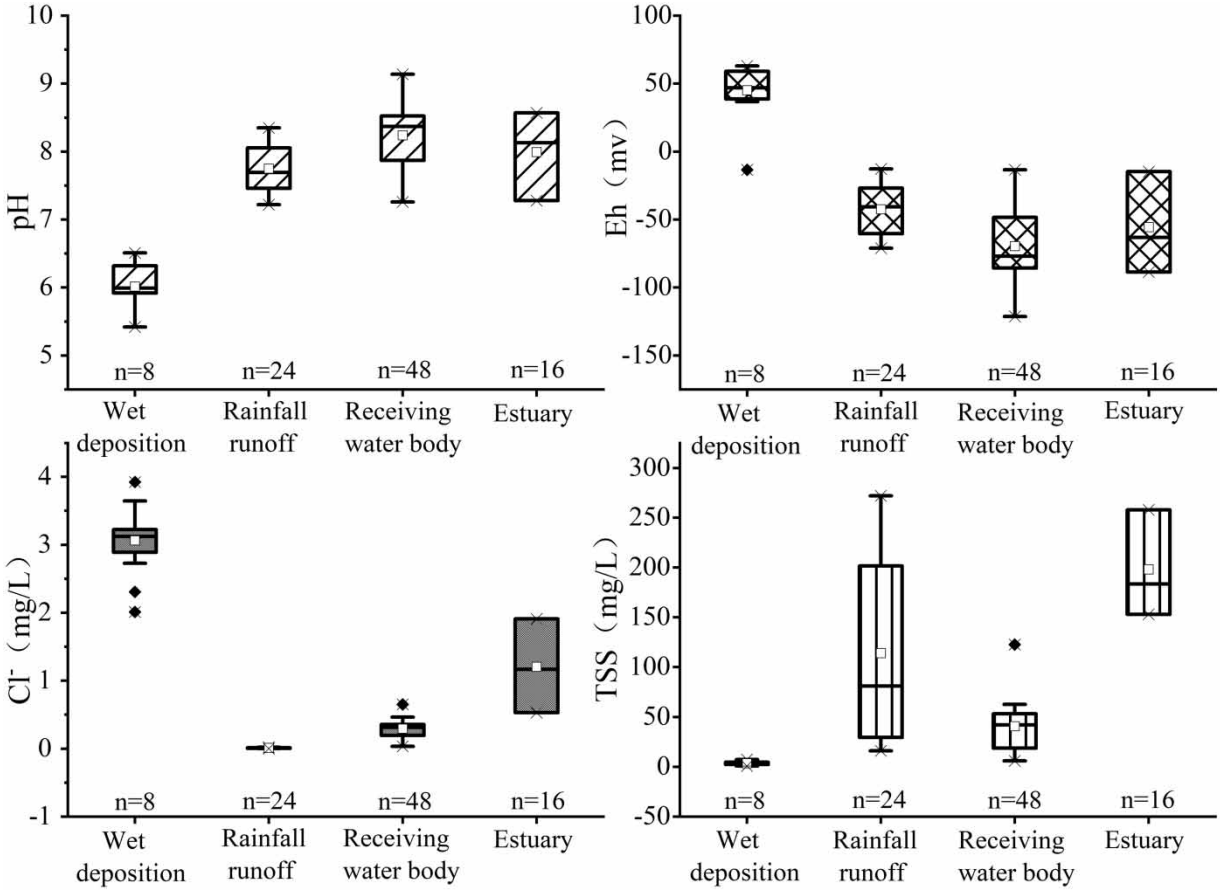

Figure 2 | Changes in the water quality parameters in the wet deposition–rainfall runoff–receiving water body–estuary water environment system.

the pollution chain decreased in the reverse order of pH. Water bodies that were less disturbed by human activities had a better oxidation state, they were more reductive, and they exhibited a high reducibility (Lin *et al.* 2018; Garaga *et al.* 2020). The proportion of days with good or excellent ambient air quality (days with AQI ≤ 100) was higher than 96% in Haikou, and the input of anthropogenic pollutants was relatively low, while wet deposition was not greatly affected by human activities. The abovementioned reasons may also be why wet deposition had the highest Eh value in the pollution chain.

The Cl^- average concentration in wet deposition, rainfall runoff, receiving water bodies, and estuaries reached 3.06 (2.01–3.93, $n = 8$) mg/L, 1.17×10^{-2} (2.9×10^{-3}–2.13×10^{-2}, $n = 24$) mg/L, 0.29 (3×10^{-2}–0.65, $n = 48$) mg/L, and 1.20 (0.53–1.91, $n = 16$) mg/L, respectively. The Cl^- average concentration decreased in the following order: wet deposition > estuary > receiving water bodies > rainfall runoff (Figure 2). Waves colliding with each other cause abundant atmospheric Cl^- salt nuclei to form over the ocean (Liu 2016). These salt nuclei drift with the wind to land many kilometers away from the coast. During rainfall, Cl^- dissolves into the rainwater, increasing the chloride ion concentration in the wet deposition. The Cl^- concentration in wet deposition on the coastal city was relatively high. (Zhang *et al.* 2019). Haikou is an island city surrounded by the sea. The precipitation air mass containing Cl^- mostly comes from the ocean. So the Cl^- content was high in wet deposition. In wet deposition in Haikou, Cl^- was mainly attributed to sea-source ions transported via the atmosphere, and not to human input. The estuary is a transitional zone between sea and land and is an ecologically interlaced zone between freshwater and ocean water. Its material and energy conversion is relatively rapid. The large Cl^- amount entering the estuary was the main reason for the high Cl^- content in the estuary.

The average concentration of total suspended solids (TSS) in wet deposition, rainfall runoff, receiving water bodies, and estuaries reached 3.48 (0.92–7.43, $n = 8$) mg/L, 114.01 (16.08–271.96, $n = 24$) mg/L, 45.63 (6.07–122.65, $n = 48$) mg/L, and 198.07 (153.00–257.80, $n = 16$) mg/L, respectively. The TSS average concentration decreased in the following order: estuary > rainfall runoff > receiving

water bodies > wet deposition (Figure 2). The TSS in wet deposition came from the atmosphere. Haikou's air quality ranked first among 74 cities including municipality cities, provincial capital cities and cities with separate plans in 2017–2018. The atmospheric particulate matter content is low, which is the main reason for the lowest TSS content in wet deposition in the entire water environment system. Estuary sediments are often resuspended into water bodies under external forces such as wind, waves and tide (Lou *et al.* 2016). At the same time, in the case of mixed saltwater and fresh water in the estuary, on the one hand, the medium- and high-salinity waters brought coarse particles, and on the other hand, polymerization between particles in low-salinity areas also readily generated coarse-grained flocs. Internal input and polymerization resulted in the highest TSS content in the estuary in the entire water environment system (Li *et al.* 2017). The study found that the strongly mixed saltwater–freshwater zone in estuary had a 'maximum turbidity zone', which was the main sedimentary area for fine-grained sediment movement in the estuary (Uncles *et al.* 2018). This was consistent with the results of a previous study in which the TSS content in the estuary reached the highest level in the pollution chain.

Changes in the Pd content in the urban water environment system

The dissolved Pd content of wet deposition, rainfall runoff, receiving water bodies, and estuaries ranged from not detected (ND) to 1.38 ng/L ($n = 8$), from 1.6 ng/L to 9.4 ng/L ($n = 24$), from 1.42 ng/L to 8.59 ng/L ($n = 48$), and from ND to 2.93 ng/L ($n = 16$), respectively. The dissolved Pd average content was the highest in rainfall runoff (4.93 ng/L), followed by that in the receiving water body (4.56 ng/L), and the lowest dissolved Pd content (0.1 ng/L) was observed in wet deposition (Figure 3).

The suspended Pd content of wet deposition, rainfall runoff, receiving water bodies, and estuaries ranged from ND to 7.7×10^{-3} ng/L ($n = 8$), from 0.06 ng/L to 3.98 ng/L ($n = 24$), from ND to 0.45 ng/L ($n = 48$), and from 1.88 to 4.46 ng/L ($n = 16$), respectively. The suspended Pd average content was the highest in the estuary (2.83 ng/L), followed by that in rainfall runoff (1.26 ng/L), and the lowest content (6×10^{-4} ng/L) occurred in wet deposition. Due to the specific physico-chemical environment of the turbidity maximum in the estuary, a ternary complex was formed on the surface of the suspended particles (Gil-Díaz *et al.* 2020), and pollutants such as Pd were easily adsorbed, which likely caused the suspended Pd content to significantly increase in the estuary.

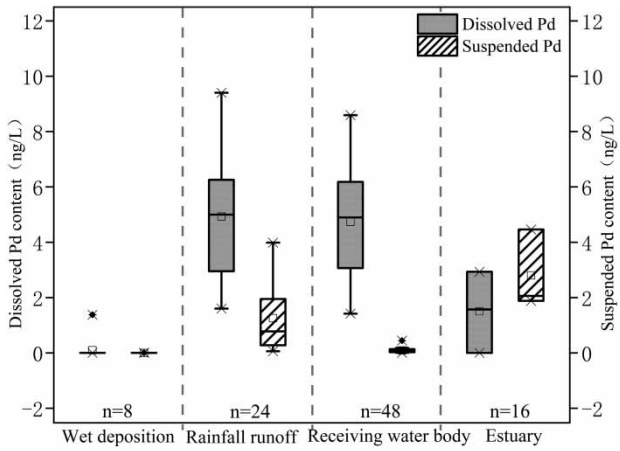

Figure 3 | Changes in Pd in the wet deposition-rainfall runoff-receiving water body-estuary water environment system.

The particle–water partition ratio can reflect the distribution of pollutants between the dissolved phase and the particle phase. Its formula is $K_d = C_s/C_w$, where C_s (mg/kg) and C_w (mg/L) are suspended and dissolved pollution content, respectively (Gogoi *et al.* 2020). The particle–water partition ratio of Pd reached 0.006, 0.26, 0.022, and 1.26 in wet deposition, rainfall runoff, receiving water bodies, and estuaries, respectively. Among them, the wet deposition Pd had a strong migration ability between the water phase and particulate matter. The estuary Pd had a high affinity for the particle phase and was easily adsorbed.

Relationship between Pd changes and water quality parameters

Studies have suggested that water quality parameters are important factors affecting the migration and transformation of pollutants in the water environment (Riedel *et al.* 1999). In the case of high pH (>8) and high turbidity, particulate matter is more likely to adsorb heavy metals (Djukić *et al.* 2016). The single-sample Kolmogorov–Smirnov test verified that the sample data conformed to the normal distribution. This study analyzed the correlations between wet deposition, rainfall runoff, receiving water body and estuary Pd content changes and water quality parameters pH, Eh, Cl^-, and TSS in the pollution chain. The results showed that the dissolved Pd was correlated with the pH, Cl^-, and TSS, and the coefficient of determination R^2 was 0.27, 0.46, and 0.15, respectively. The suspended Pd was only correlated with Cl^- and TSS, and the values of R^2 were 0.13 and 0.57,

respectively. In addition, there was a strong correlation ($R^2 =$ 0.94, 0.58, and 0.49, respectively) between water quality parameters pH, Eh, and Cl^- but a weak or moderate correlation ($R^2 = 0.09$, 0.08, and 0.17, respectively) with TSS (Table 2).

Zereini *et al.* (2012) proposed that the pH solubility was strongly dependent on pH. Estuary trace metal solid–liquid partitioning also affects the pH; that is, the increase in pH enhanced the distribution of trace metals in the sediment and could promote the transfer of trace metal elements to the sediment solid phase (Liu *et al.* 2019). This study found that the dissolved Pd was moderately related to the pH ($r = 0.52$, $p < 0.05$) and that the suspended Pd was not related to the pH ($r = 0.16$) (Table 2). The relationship between the dissolved Pd and pH was close to the results of Zereini, but the pH effect of Pd was not significant.

The adsorption and desorption of heavy metals at interfaces are often related to changes in Eh (Riedel *et al.* 1999). However, the analysis data showed that the dissolved and suspended Pd and Eh levels in the wet deposition–rainfall runoff–receiving water body–estuary pollution chain were not related ($r = 0.14$, 0.13), and there was no similarity with the results of heavy metals.

The change in salinity would not only change the occurrence form of metal ions but also change the ionic strength of water, which would affect the migration of heavy metals and other elements at solid–liquid interfaces to change their distribution between the dissolved and solid states (Chou *et al.* 2018). This study found that Cl^- had a very notable negative correlation with the dissolved Pd ($r = -0.68$, $p < 0.05$) and a weak negative correlation with the suspended Pd ($r = -0.37$, $p < 0.05$), which is consistent with the research of Zhang (2013). In addition, the wet deposition Cl^- content in the pollution chain was the highest, but the particle–water partition ratio of Pd was the lowest, which indicated that as the salinity increased, the dissolved Pd content increased. Mashio *et al.* (2016) proposed that the dissolved Pt concentration in PGEs increased sharply in high-salinity regions, which was in line with the Pd results in this study.

TSS was weakly correlated with the dissolved Pd ($r = 0.39$, $p < 0.05$) and strongly correlated with the suspended Pd ($r = 0.79$, $p < 0.05$). The suspended Pd was mainly adsorbed onto TSS and would be desorbed from TSS to become dissolved Pd. The TSS content directly affected the Pd concentration, resulting in the correlation between TSS and the dissolved and suspended Pd. The TSS surface structure characteristics, specific surface area, and particle size might significantly impact Pd adsorption or desorption (Horowitz & Elrick 1987).

Among the four physical and chemical factors, Cl^- and TSS were the most closely related to Pd in the pollution chain. Studies have suggested that although the pH, Eh, Cl^- and other factors might play a key role in different environments, they often have a synergistic effect on the presence of pollutants (Zheng *et al.* 2013). In this study, correlation analysis found that although individual factors such as the pH, Cl^-, and TSS had certain effects on Pd in the wet deposition–rainfall runoff–receiving water body–estuary pollution chain, the probability of strong correlations was not high. In particular, Eh was not related to the dissolved nor suspended Pd content, which might also be a synergistic effect of the various factors on Pd.

CONCLUSION

(1) In the urban water environment system, the average pH decreased in the following order: receiving water body (8.23) > estuary (8.13) > rainfall runoff (7.75) > wet deposition (6.23). The average Eh decreased in the following order: wet deposition (45.19 mV) > rainfall runoff (−42.38 mV) > estuary (−55.5 mV) > receiving water body (−71.74 mV). The Cl^- average concentration decreased in the following order: wet deposition

Table 2 | Relationship between Pd and the various physical and chemical factors in the urban water environment system

Correlation (r)	pH	Eh	Cl^-	TSS	Dissolved Pd	Suspended Pd
pH	1.00	−0.97	−0.76	0.31	0.52	0.16
Eh		1.00	0.70	−0.28	0.14	0.13
Cl^-			1.00	−0.42	−0.68	−0.21
TSS				1.00	0.39	0.76
Dissolved Pd					1.00	0.12
Suspended Pd						1

(3.06 mg/L) > estuary (1.2 mg/L) > receiving water bodies (0.29 mg/L) > rainfall runoff (1.17×10^{-2} mg/L). The average TSS decreased in the following order: estuary (198.07 mg/L) > rainfall runoff (114.01 mg/L) > receiving water bodies (45.63 mg/L) > wet deposition (3.48 mg/L). There were significant differences in the water quality parameters (pH, Eh, Cl^-, TSS) of wet deposition, rainfall runoff, receiving water bodies, and estuary.

(2) The dissolved Pd average content was the highest in rainfall runoff (4.93 ng/L), followed by that in the receiving water body (4.56 ng/L), and it was the lowest in wet deposition (0.1 ng/L). The suspended Pd average content was the highest in the estuary (2.83 ng/L), followed by that in rainfall runoff (1.26 ng/L), and it was the lowest in wet deposition (6×10^{-4} ng/L). The particle–water partition ratio of the estuary Pd was the highest, followed by that of the rainfall runoff Pd, and the particle–water partition ratio of the wet deposition Pd was the lowest. The decreasing order of particle–water partition ratio was consistent with suspended Pd, which could better reflect the adsorption capacity of suspended matter to Pd.

(3) The dissolved Pd was correlated with the pH, Cl^-, and TSS ($r = 0.52$, -0.68, and 0.39, respectively, $p < 0.05$), but the suspended Pd was only correlated with Cl^- and TSS ($r = -0.37$ and 0.76, respectively, $p < 0.05$). Cl^- and TSS were the most closely related to Pd in the pollution chain. Although individual factors such as pH, Cl^-, and TSS had some influence on Pd in the wet deposition–rainfall runoff–receiving water body–estuary pollution chain, the probability of strong correlations was not high. In particular, Eh was not related to the dissolved nor suspended Pd ($r = 0.14$ and 0.13, respectively), which might also be a synergistic effect of the various factors on Pd.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (41867060), the Key Research, Development Program of Hainan Province (ZDYF2019131), and Postgraduate Scientific Research and Innovation Project of Hainan (Hys2019-241). We thank the 2014 undergraduates at the College of Geography and Environmental Science, Hainan Normal University, Chao Lan, Changdong Zou, Xing Yang, Linsheng He, Qianqian Fu, Mengchen Shen; 2015 undergraduate Siying Wang; and other students, who helped complete the sampling work.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

REFERENCES

Birke, M., Rauch, U., Stummeyer, J., Lorenz, H. & Keilert, B. 2018 A review of platinum group element (PGE) geochemistry and a study of the changes of PGE contents in the topsoil of Berlin, Germany, between 1992 and 2013. *Journal of Geochemical Exploration* **187**, 72–96. https://doi.org/10.1016/j.gexplo.2017.09.005.

Chou, P.-I., Ng, D.-Q., Li, I.-C. & Lin, Y.-P. 2018 Effects of dissolved oxygen, pH, salinity and humic acid on the release of metal ions from PbS, CuS and ZnS during a simulated storm event. *Science of the Total Environment* **624**, 1401–1410. https://doi.org/10.1016/j.scitotenv.2017.12.221.

Dahlheimer, S. R., Neal, C. R. & Fein, J. B. 2007 Potential mobilization of platinum-group elements by siderophores in surface environments. *Environmental Science & Technology* **41** (3), 870–875. http://doi.org/10.1021/es0614666.

Djukić, A., Lekić, B., Rajaković-Ognjanović, V., Veljović, D., Vulić, T., Djolić, M., Naunov, Z., Despotović, J. & Prodanović, D. 2016 Further insight into the mechanism of heavy metals partitioning in stormwater runoff. *Journal of Environmental Management* **168**, 104–110. https://doi.org/10.1016/j.jenvman.2015.11.035.

Fu, B., Liu, Y. Y., Zhao, Z. Z., Zhang, L., Wu, D. & Liu, H. F. 2018 Dissolved palladium in heavy traffic location runoff: dynamic variation and influencing factors. *Urban Water Journal* **15** (9), 880–887. https://doi.org/10.1080/1573062X.2019.1579348.

Garaga, R., Chakraborty, S., Zhang, H., Gokhale, S., Xue, Q. & Kota, S. H. 2020 Influence of anthropogenic emissions on wet deposition of pollutants and rainwater acidity in Guwahati, a UNESCO heritage city in Northeast India. *Atmospheric Research* **232**, 104683. https://doi.org/10.1016/j.atmosres.2019.104683.

Gil-Díaz, T., Schäfer, J., Keller, V., Eiche, E., Dutruch, L., Mößner, C., Markus, L. & Eyrolle, F. 2020 Tellurium and selenium sorption kinetics and solid fractionation under contrasting estuarine salinity and turbidity conditions. *Chemical Geology* **532**, 119370. https://doi.org/10.1016/j.chemgeo.2019.119370.

Gogoi, A., Taki, K. & Kumar, M. 2020 Seasonal dynamics of metal phase distributions in the perennial tropical (Brahmaputra) river: environmental fate and transport perspective. *Environmental Research* **183**, 109265. https://doi.org/10.1016/j.envres.2020.109265.

Horowitz, A. J. & Elrick, K. A. 1987 The relation of stream sediment surface area, grain size and composition to trace element chemistry. *Applied Geochemistry* **2**, 437–451. https://doi.org/10.1016/0883-2927(87)90027-8.

Howland, R. J. M. 2000 Distributions and seasonal variability of pH and alkalinity in the Tweed Estuary, UK. *Science of the Total Environment* **251**, 125–138. https://doi.org/10.1016/S0048-9697(00)00406-X.

Huber, M., Welker, A. & Helmreich, B. 2016 Critical review of heavy metal pollution of traffic area runoff: occurrence, influencing factors, and partitioning. *Science of the Total Environment* **541**, 895–919. https://doi.org/10.1016/j.scitotenv.2015.09.033.

Li, D., Li, Y. & Xu, Y. 2017 Observations of distribution and flocculation of suspended particulate matter in the Minjiang River Estuary, China. *Marine Geology* **387**, 31–44. https://doi.org/10.1016/j.margeo.2017.03.006.

Lin, X., He, L., Zhang, R., Guo, X. & Li, H. 2018 Rainwater in Guangzhou, China: oxidizing properties and physicochemical characteristics. *Atmospheric Pollution Research* **101**, 303–312. S1309104218301533. https://doi.org/10.1016/j.apr.2018.08.005.

Liu, J. 2016 *Analysis of Water Quality Characteristics of Atmospheric Precipitation in Beijing Urban Area*. PhD thesis, Ji Nan University. DOI: CNKI:CDMD:2.1016.257873.

Liu, Y. Y., Liu, M. & Liu, H. F. 2007 Research on urban soil properties and pollution in Urumqi. *Research on Arid Areas* **24** (1), 66–69. https://doi.org/CNKI:SUN:GHQJ.0.2007-01-011.

Liu, Y. Y., Tian, F. F., Liu, C. & Zhang, L. 2015 Platinum group elements in the precipitation of the dry region of Xinjiang and factors affecting their deposition to land: the case of Changji City, China. *Atmospheric Pollution Research* **6** (2), 178–183. https://doi.org/10.5094/APR.2015.021.

Liu, M., Chen, J., Sun, X., Hu, Z. & Fan, D. 2019 Accumulation and transformation of heavy metals in surface sediments from the Yangtze River estuary to the East China Sea shelf. *Environmental Pollution* **245**, 111–121. https://doi.org/10.1016/j.envpol.2018.10.128.

Lou, S., Huang, W., Liu, S., Zhong, G. & Johnson, E. 2016 Hurricane impacts on turbidity and sediment in the Rookery Bay National Estuarine Research Reserve, Florida, USA. *International Journal of Sediment Research* **31** (4), 330–340. https://doi.org/10.1016/j.ijsrc.2016.06.006.

Ma, Q., He, C. & Wu, J. G. 2016 Behind the rapid expansion of urban impervious surfaces in China: major influencing factors revealed by a hierarchical multiscale analysis. *Land Use Policy* **59**, 434–445. https://doi.org/10.1016/j.landusepol.2016.09.012.

Mashio, A. S., Obata, H., Tazoe, H., Tsutsumi, M., Ferrer i Santos, A. & Gamo, T. 2016 Dissolved platinum in rainwater, river water and seawater around Tokyo Bay and Otsuchi Bay in Japan. *Estuarine, Coastal and Shelf Science* **180**, 160–167. https://doi.org/10.1016/j.ecss.2016.07.002.

Riedel, G. F., Sanders, J. G. & Osman, R. W. 1999 Biogeochemical control on the flux of trace elements from estuarine sediments: effects of seasonal and short-term hypoxia. *Marine Environmental Research* **47**, 349–372. https://doi.org/10.1016/s0141-1136(98)00125-1.

Suoranta, T., Niemelä, M., Poikolainen, J., Piispanen, J., Bokhari, S. N. H., Meisel, T. & Perämäki, P. 2016 Active biomonitoring of palladium, platinum, and rhodium emissions from road traffic using transplanted moss. *Environmental Science & Pollution Research* **23** (16), 1–12. http://dx.doi.org/10.1007/s11356-016-6880-1.

Sutherland, R. A., Pearson, G. D., Ottley, C. J. & Ziegler, A. D. 2015 Platinum-group elements in urban fluvial bed sediments – Hawaii. In: *Platinum Metals in the Environment*. Springer, Berlin, Germany. https://doi.org/10.1007/978-3-662-44559-4_12.

Uncles, R. J., Hooper, T., Stephens, J. A. & Harris, C. 2018 Seasonal variability of turbidity, salinity, temperature and suspended chlorophyll in a strongly tidal sub-estuary: The Lynher Marine Conservation Zone. *Estuarine, Coastal and Shelf Science* **212**, 253–264. https://doi.org/10.1016/j.ecss.2018.07.017.

Wiseman, C. L. S. & Zereini, F. 2009 Airborne particulate matter, platinum group elements and human health: a review of recent evidence. *Science of the Total Environment* **407** (8), 2493–2500. https://doi.org/10.1016/j.scitotenv.2008.12.057.

Xu, H., Xiao, X. B., Tang, W. H., Ge, C. J. & Yang, Y. 2013 Study on the characteristics of antibiotic content in the surface water environment of Haikou City. *Environmental Science and Technology* **36** (9), 60–65. https://doi.org/10.3969/j.issn.1003-6504.2013.09.013.

Zereini, F., Wiseman, C. L. S. & Wilhelm, P. 2012 In vitro investigations of platinum, palladium, and rhodium mobility in urban airborne particulate matter (PM10, PM2.5, and PM1) using simulated lung fluids. *Environmental Science & Technology* **46** (18), 10326–10333. https://dx.doi.org/10.1021/es3020887.

Zereini, F., Wiseman, C. L. S., Poprizki, J., Albers, P., Schneider, W. & Leopold, K. 2016 Assessing the potential of inorganic anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) to increase the bioaccessibility of emitted palladium in the environment: experimental studies with soils and a Pd model substance. *Environmental Pollution Part B* **220**, 1050–1058. http://dx.doi.org/10.1016/j.envpol.2016.11.039.

Zhang, X. L. 2013 *Study on the Distribution Characteristics and Influencing Factors of Heavy Metals in the Yangtze River Estuary, Yellow River Estuary and Adjacent Sea Areas*. PhD thesis, Ocean University of China. https://doi.org/10.7666/d.D326582.

Zhang, E., Gao, S., Savenije, H. H. G., Si, C. & Cao, S. 2019 Saline water intrusion in relation to strong winds during winter cold outbreaks: North Branch of the Yangtze Estuary. *Journal of Hydrology* **574**, 1099–1109. https://doi.org/10.1016/j.jhydrol.2019.04.096.

Zheng, S., Wang, P., Wang, C., Hou, J. & Qian, J. 2013 Distribution of metals in water and suspended particulate matter during the resuspension processes in Taihu Lake sediment, China. *Quaternary International* **286**, 94–102. https://doi.org/10.1016/j.quaint.2012.09.003.

Zhou, Y., Yao, X., Zhang, Y., Shi, K., Zhang, Y., Jeppesen, E., Gao, G., Zhu, G. & Qin, B. 2017 Potential rainfall-intensity and pH-driven shifts in the apparent fluorescent composition of dissolved organic matter in rainwater. *Environmental Pollution* **224**, 638–648. https://doi.org/10.1016/j.envpol.2017.02.048.

First received 28 January 2020; accepted in revised form 12 June 2020. Available online 26 June 2020