

Platinum-group and other traffic-related heavy metal contamination in road sediment, Guangzhou, China

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Abstract

Purpose Human exposure to particulate matter emitted from on-road motor vehicles includes complex mixtures of heavy metals from tyres, brakes, part wear, and resuspended road sediment. The purpose of this study was to determine the concentrations of 14 platinum-group and other traffic-related heavy metals in road sediment within the metropolitan area of Guangzhou, China, with a view to identifying their sources and assessing the extent of anthropogenic influence on heavy metal contamination of road sediment. **Materials and methods** Thirty-five samples of road sediment were collected. The concentrations of Cr, Mn, Ni, Cu, Zn, La, Ce, Mo, Cd, Pb, Ba, and Rh were measured by inductively coupled plasma–mass spectrometry. Pt and Pd were analyzed by isotopic dilution–inductively coupled plasma–mass spectrometry. Multivariate statistical analysis and enrichment factor methods were employed to identify the sources of these heavy metals and to assess anthropogenic influences on their occurrence.

Results and discussion The mean concentrations of Pt, Pd, Rh, Cr, Mn, Ni, Cu, Zn, La, Ce, Mo, Cd, Pb, and Ba in the

road sediment samples were 68.24, 93.15, 23.85, 147.5, 712.3, 47.24, 177.5, 1254, 47.50, 96.62, 4.91, 3.00, 198.1, and 641.3 ng g⁻¹, respectively. Very weak to significant linear positive correlations were found among the various heavy metals. The elemental composition of road sediment was dominated by five principal components. Three clusters were identified through cluster analysis, and enrichment factors were calculated relative to soils in China. The sources and degree of contamination of the heavy metals are discussed based on the results.

Conclusions The mean concentrations of heavy metals are higher than background values, especially for Pt, Pd, Rh, Cd, and Zn. Four main sources are identified: (1) Pt, Pd, and Rh were derived from traffic sources; (2) La, Ce, Mn, and Ba were derived mainly from natural sources; (3) Cr, Ni, Cu, Mo, Cd, and Pb showed mixed traffic–industry sources; and (4) Zn originated mainly from industrial sources. Enrichment factor analysis supported this source identification and further indicated that contamination of road sediment in Guangzhou is extremely high for Pt, Pd, and Rh; moderate to very high for Cd, Zn, Pb, Cu, and Mo; and minimal for Cr, Ni, La, Ce, and Ba.

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1 Introduction

The worldwide production of platinum-group elements (PGEs) has risen steadily over the past three decades to meet demand from the automotive, chemical, dental, electronic, glass, pharmaceutical, and petroleum industries (Jollie 2010). In particular, the metals platinum (Pt),

palladium (Pd), and rhodium (Rh) are widely used in vehicle exhaust catalysts (VECs) to convert noxious gases into more environmentally friendly forms. While VECs help improve air quality in general, they have become a primary source of Pt, Pd, and Rh in the environment. This has led to increased concentrations of these metals in a variety of environmental media. For example, concentrations as high as 2,522 ng g⁻¹ of Pt and 516 ng g⁻¹ of Pd have been recorded in road sediment (Gómez et al. 2001; Leopold et al. 2008).

In addition to PGEs, other elements such as Ce, La, Mo, and Ni are used in vehicle exhaust converters (Baldanza et al. 2000; Gandhi et al. 2003; Morcelli et al. 2005; Zotin et al. 2005). These metals can be emitted to the atmosphere (in small quantities) together with particles from the washcoat component of catalytic converters as a result of chemical and physical stresses such as sintering and thermal shock (Artelt et al. 1999; Palacios et al. 2000). Other traffic-related elements (TRE) found in city environments include Ba, Cd, Cr, Cu, Mn, Zn, and Pb. The sources of these heavy metals include exhaust emissions, lubrication losses, and the degradation of vehicle tyres, brake linings, and motorway surfaces (Hares and Ward 1999). For example, Cu, which is used as a component in brakepad materials, is a public health concern because the dust produced from brake wear (particle size of 1–10 µm) is partially inhalable (Birmili et al. 2006). Ni is associated with vehicular emissions, since it is used as a fuel additive (Park and Kim 2005) and is used in automotive catalytic converters to minimize H₂S emissions (Zotin et al. 2005). Pb can also be emitted from the combustion of leaded gasoline (Zheng et al. 2004), mechanical attrition (Salma and Maenhaut 2006), and the incineration of vehicle tires (Gieré et al. 2006). In 1997, metropolitan cities including Beijing, Shanghai, and Guangzhou began to use unleaded gasoline, and in 2000, China prohibited the sale and use of leaded gasoline.

Most of the traffic-related heavy metals are non-essential nutrients for humans and animals. Exposure to these metals has been associated with adverse health effects. Indications of the acute toxicity of several PGE-chlorinated salts and evidence of DNA damage due to PGE exposure have been observed both *in vitro* and *in vivo* (Gagnon et al. 2006). Although some traffic-related heavy metals, such as Cu, Zn, and Mn, are essentially trace nutrients in humans and animals, excessive exposure has long been known to elicit toxicity in humans of all ages. For example, Mn presents a conundrum for risk assessment because it is both an essential trace element and a potent neurotoxicant (Weiss 2006). Its neurotoxic properties emerge almost exclusively from inhalation exposure, although it has been suggested that

children are at risk of Mn-induced neurotoxicity via drinking water (Wasserman et al. 2006), and infant mortality may be related to Mn exposure (Hafeman et al. 2007).

Guangzhou, which is the capital of Guangdong Province in China and is part of the Pearl River Delta (PRD) region, is the largest industrial center in China and one of the fastest growing cities. The city has experienced a tremendous increase in motorized traffic volume since 2000, with above 1.5 million vehicles on the road. Rapid economic development over the past three decades has brought great prosperity to the region, but has also led to environmental problems. The decline in regional environmental quality since the late 1980s has spurred extensive research in the area, including that of the concentration, distribution, partitioning, sources, and enrichment of heavy metal contaminants (e.g., Wong et al. 2003; Duzgoren-Aydin et al. 2006a,b; Duzgoren-Aydin 2007; Lee et al. 2007; Li et al. 2009). In particular, recent studies of road sediment in Guangzhou have reported that the level and extent of Zn contamination is more severe and widespread than that for other trace metals such as Cd, Cu, and Pb (Duzgoren-Aydin et al. 2006b).

Road sediment (also called “street dust” or “road dust”) is a complex mixture of particles from a number of natural and anthropogenic sources, including tyre and brake wear; exhaust fumes; road surface abrasion; corrosion particles from vehicles; and particles from various diffuse sources, such as waste incineration, fossil-fuel power plants, and building materials. Heavy metals can accumulate in road sediment through atmospheric deposition. As a sink or source, road sediment is therefore a good indicator of the level and extent of heavy metal accumulation in the surface environment (Duzgoren-Aydin et al. 2006a; Taylor and Owens 2009). The advantages of using road sediment as a source of environmental information include its ubiquitous nature, ease of sampling, strong association with automobile emissions, and its relationship with non-point-source pollution (Sutherland 2003). Many studies of PGEs or heavy metal concentrations have been carried out using road sediment (e.g., Zereini et al. 2001; Leopold et al. 2008; Joshi et al. 2009; Prichard et al. 2009; Qiu et al. 2009; Lu et al. 2010; Apeageyi et al. 2011), but few have examined platinum-group and other traffic-related heavy metals (e.g., Pratt and Lottermoser 2007; da Silva et al. 2008).

The primary objectives of this preliminary study were to (1) determine the concentrations of 14 platinum-group and other traffic-related heavy metals in road sediment collected from different urban settings within the metropolitan area of Guangzhou, China; (2) identify the natural or anthropogenic sources of these heavy metals using multivariate statistical analysis; and (3) assess the extent of anthropogenic influence on heavy metal contamination of road sediment using enrichment factors (EFs).

2 Materials and methods

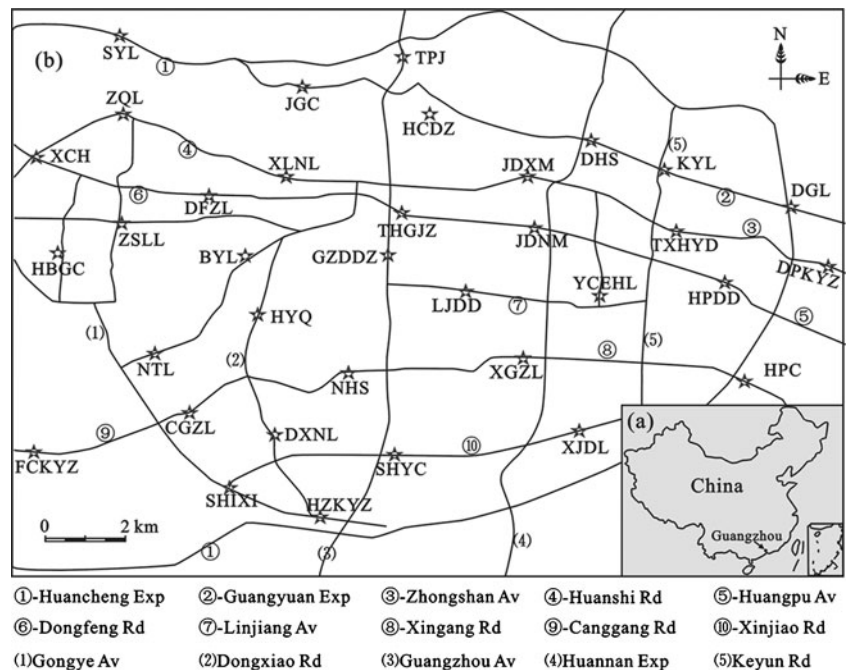
2.1 Reference materials and equipment

Three reference materials with different lithological characteristics were analyzed to assess the accuracy of the analytical method used to detect PGEs, as described in Section 2.3: (1) stream sediment from the National Research Center for Geoanalysis, China (GPt-2); (2) basalt from the US Geological Survey (BHVO-2); and (3) altered peridotite from the Canadian Certified Reference Materials Project (WPR-1). Two isotopic spikes (Pd and Pt metal power enriched with ^{105}Pd and ^{194}Pt , respectively) were obtained from Oak Ridge National Laboratory, USA. Cation resin AG50W-X8 (200–400 mesh) was obtained from Bio-Rad Laboratories Inc., USA, and *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) was obtained from Aladdin Reagent Inc., China. Pure water from a Milli-Q system (Millipore Corp., Millford, USA) and acids (HCl, HNO_3 , and HF) from a sub-boiling distillation system were also used. A quadrupole inductively coupled plasma–mass spectrometer (ICP-MS; Elan 6000, PE Inc.) was used for the analysis of PGEs and other heavy metal elements.

2.2 Sample collection and pretreatment

Guangzhou has a mild subtropical climate with hot and humid summers (April–September) and relatively cool and dry winters (October–March). Mean temperatures in July and January are 28.5 and 13.3 °C, respectively. Annual total rainfall is approximately 1,680 mm, most of which falls between April and September (Duzgoren-Aydin et al. 2006b).

Fig. 1 Regional map of China showing the location of Guangzhou (a) and sampling sites (b)



Samples were collected from 35 sites in the metropolitan area of Guangzhou during 21–23 January 2009 (Fig. 1). The sampling period was preceded by 16 consecutive sunny days in Guangzhou. The detailed sampling locations and average daily traffic volumes are listed in the Electronic Supplementary Material Table S1. All the samples were collected along the curb in streets with various traffic volumes using a dust collector (FC8262, Philips Inc.). The sampling width from the curb, length along the curb, and area were 20–40 cm, 2–6 m, and 0.5–2.0 m², respectively. A different dust bag was used at each location to avoid cross-contamination of the samples. With the exception of one location (the intersection between Erheng Road and New Street, Yuan Village), the roads are wide, with 4–12 traffic lanes. The average daily traffic at the sampling sites was estimated to range from 5,000 to 80,000 vehicles.

The collected road dust samples were dried in an oven at 60 °C for 1 day and then sieved (< 2 mm) to remove large plant and plastic debris, gravel-sized materials, and cigarette butts. They were further sieved to isolate the <0.075 mm grain-size fraction for analysis, based on the high contribution of the fine grain-size fraction to airborne particulate matter and transport of material into the water system (Owens et al. 2011). All samples were homogenized and ground with a pestle and agate mortar, and kept in a desiccator prior to chemical digestion.

2.3 Analytical methods and quality control

All of the heavy metal analysis was performed at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China. A strong acid digestion

method was used to dissolve the samples. For this, about 40 mg samples of road sediment from each site were dissolved in distilled HF+HNO₃+HClO₄ in 15 ml Savillex® Teflon screw-cap beakers and high-pressure Teflon bombs at 190 °C for 2 days. Samples were then dried and subsequently diluted to 80 ml with 3 % HNO₃ solution. Heavy metal concentrations were measured by ICP-MS with a Perkin-Elmer Elan 6000 mass spectrometer. A blank (control) solution (no road sediment) was prepared, and the total procedural blank was <50 pg for all heavy metal elements. Rhodium was used as an internal standard to correct for matrix effects and instrument drift. Precision for all heavy metal elements was estimated to be 5 % (2σ), and accuracy was better than 5 % (2σ) for analyses of the Chinese standard materials GSD-9, GSD-10, and GSD-12.

Pt and Pd concentrations were measured by isotopic dilution–inductively coupled plasma–mass spectrometry with a Perkin-Elmer Elan 6000 mass spectrometer. Rh was measured by external standard–inductively coupled plasma–mass spectrometry. Pt, Pd, and Rh were extracted quantitatively from the samples (1.0–2.0 g) into aqua regia in Carius tubes, and the spike and sample were isotopically equilibrated at 230 °C in an oven for 2 days. Pt, Pd, and Rh were separated from the sample matrix by cation exchange chromatography (AG50W-X8) and solvent extraction (BPHA in CCl₄). This analytical procedure has the potential to greatly reduce the total procedural blanks (Pearson and Woodland 2000). The digested sample solutions were transferred into 22 ml Savillex® PFA standard vials and dried before adding 2 ml of 6 mol l⁻¹ HCl acid, and kept at 100 °C for 2 h. Samples were then re-dried, another 5 ml of 1.0 mol l⁻¹ HCl acid was added, and the samples were kept at 100 °C for a further 2 h. Finally, 5 ml of Milli-Q water was added, and the diluted solutions were filtrated through a 0.45-μm microporous filter membrane, and passed through the cation exchange resin. Subsequently, 30 ml of 0.5 mol l⁻¹ HCl acid was used to elute Pt, Pd, and Rh from the matrix. Samples were further purified by solvent extraction with BPHA in chloroform solution (Shinotsuka and Suzuki 2007) to remove interfering Mo, Zr, and Hf anion complexes. All aspects of chemical treatment were performed in a super-clean laboratory to ensure low blanks.

The three reference materials (GPt-2, BHVO-2, and WPR-1; see Section 2.1) were analyzed to assess the accuracy of the analytical method. The total procedural blanks of the analytical method were controlled by adding a blank to each batch of experiments. The results for the reference materials were consistent with the Pt, Pd, and Rh concentrations, and were in excellent agreement with certified values and previous results. The blank levels (the average concentration of five procedural reagent blanks) of Pt, Pd, and Rh were 2, 7, and 3 pg, respectively. The instrumental quantification limits of Pt, Pd, and Rh (calculated as three

times the standard deviation of ion counts obtained from the 3 % HNO₃ solution measured 12 times, divided by the sensitivity determined using the 10 ng ml⁻¹ PGE standard solution) were 3, 10, and 4 pg ml⁻¹, respectively. Detailed analytical results for the reference materials and procedural blanks are described elsewhere (Li et al. 2011). The instrumental quantification limits (unit, 10⁻⁹) of Cr, Mn, Ni, Cu, Zn, La, Ce, Mo, Cd, Pb, Ba, and Sc (calculated as three times the standard deviation of the procedural reagent blanks measured 10 times) were 99.0, 7.8, 27.6, 8.5, 52.0, 0.5, 0.5, 2.6, 2.7, 10.9, 6.8, and 25.6, respectively. Pt and Pd concentrations were calculated from measured ¹⁹⁵Pt/¹⁹⁴Pt and ¹⁰⁶Pd/¹⁰⁵Pd values, and a Pd–Pt standard solution was used to correct for instrumental mass fractionation. Rh concentrations were obtained using the external standard method. Isobaric interference on Pd masses was corrected by monitoring ²⁰⁰Hg and ¹¹¹Cd. It was also possible to identify potential polyatomic interference in Pd or Rh from CuAr, ZnAr, RbO, SrO, YO, and ZrO molecular species by measuring ¹⁰⁸Pd and other metallic isotopes, e.g., ⁶³Cu, ⁶⁴Zn, ⁸⁵Rb, ⁸⁵Sr, ⁸⁹Y, ⁹⁰Zr, and ⁹⁵Mo (Simitchiev et al. 2008). ¹⁸⁰Hf was monitored to assess the potential interference of HfO species on Pt (Simitchiev et al. 2008).

2.4 Statistical analysis

SPSS for Windows (version 13.0, SPSS Inc., USA) was used for descriptive, correlation, principal component, and cluster analyses. Descriptive data were obtained, including the mean, median, minimum and maximum concentrations, standard deviation (SD), coefficient of variation (CV), and skewness. Coefficients of variation (being equal to SD/mean) were used to assess the degree of discrete distribution of the different metal element concentrations and to indicate indirectly the activity of the selected element in the environment. In addition, correlation coefficients were calculated to determine the relationships among the elements.

Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies (e.g., Liu et al. 2003; Han et al. 2006; Lu et al. 2010). PCA is often used to reduce data and to extract latent factors (i.e., principal components, PCs) to analyze relationships among the observed variables. If there are large differences in the standard deviations of variables, PCA results vary considerably depending on whether the covariance or correlation matrix is used (Farnham et al. 2003). To aid interpretation, PCA with VARIMAX normalized rotation was applied, which could maximize the variance of the factor loadings across variables for each factor. Typically, factor loadings of >0.71 are regarded as excellent and <0.32 as very poor (García et al. 2004). When PCA with VARIMAX normalized rotation is performed, each PC score contains

information of all of the metal elements combined into a single number, while the loadings indicate the relative contribution of each element to the score. In this study, because of the large range of concentrations of the trace elements, PCA was applied to the correlation matrix, and each variable was normalized to unit variance to ensure that each variable made an equal contribution. In addition, all the principal factors extracted from the variables were retained with eigenvalues >1.0, as suggested by the Kaiser criterion (Kaiser 1960).

Cluster analysis was performed to further classify elements from different sources on the basis of similarities between their chemical properties. Hierarchical cluster analysis assisted in identifying relatively homogeneous groups of variables, using an algorithm that starts with each variable in a separate cluster and combines clusters until only one is left. As the variables have large differences in scaling, standardization was performed before computing proximities, which can be done automatically by the hierarchical cluster analysis procedure. A dendrogram was constructed to assess the cohesiveness of the clusters formed, in which correlations among elements are readily apparent. The CA is complementary to PCA.

2.5 Enrichment factor

The enrichment factor (EF) can be used to differentiate heavy metals originating from human and natural sources and, therefore, to assess the degree of anthropogenic influence on heavy metal contamination. One technique in this regard is normalization of a tested element against a reference element such as Al, Fe, Mn, Sc, Ti, Zr, etc. (Reimann and Caritat 2000; Hernandez et al. 2003; Conrad and Chisholm-Brause 2004; Han et al. 2006). Sc was chosen as the reference element in this study based on the descriptive statistical results and its geochemical properties. EFs were calculated using the modified formula suggested by Buat-Menard and Chesselet (1979):

$$EF(i) = \left[\frac{C(i)_{\text{sample}}/C(X)_{\text{sample}}}{[C(i)_{\text{reference}}/C(X)_{\text{reference}}]} \right]$$

where $C(i)_{\text{sample}}$ is the concentration of the examined element in road sediment, $C(X)_{\text{sample}}$ is the concentration of the reference element in road sediment, $C(i)_{\text{reference}}$ is the background value of the examined element in soil, and $C(X)_{\text{reference}}$ is the background value of the reference element in soil.

EFs close to 1 indicate a crustal origin, while those >10 are considered to have a non-crustal source (Liu et al. 2003). Furthermore, EFs can be used to classify the degree of heavy metal contamination using five categories (Sutherland 2000): (1) $EF < 2$ (depletion to minimal enrichment); (2) $EF = 2-5$ (moderate enrichment); (3) $EF = 5-20$ (significant

enrichment); (4) $EF = 20-40$ (very high enrichment); and (5) $EF > 40$ (extremely high enrichment).

3 Results and discussion

3.1 Heavy metal concentrations

Table 1 summarizes the descriptive statistical data for platinum-group and other traffic-related heavy metal concentrations measured in road sediment ($n=35$) from Guangzhou, as well as background (reference) values for soils in China (Chi and Yan 2007). Despite the introduction of vehicle exhaust catalysts in China some 20 years after that in other developed countries, PGE concentrations in road sediment from Guangzhou are similar to, or slightly higher than, those reported in other studies (e.g., Leopold et al. 2008; Sutherland et al. 2008; Prichard et al. 2009). However, the concentration of other traffic-related trace metals was generally higher for the Guangzhou samples than found elsewhere (e.g., Christoforidis and Stamatis 2009; Apeagyei et al. 2011; Duong and Lee 2011), particularly for Cd, Cu, Pb, and Zn.

Compared with background values in soil, mean concentrations of Pt, Pd, and Rh were much higher in road sediment from Guangzhou. For example, the mean concentration of Rh in road sediment was more than 1,400 times higher than the reference value. Ratios of mean concentrations in road sediment to corresponding reference values (in soil), in decreasing order, were $Rh > Pd > Pt > Cd > Zn > Pb > Cu > Mo > Cr > Ni$. In contrast, the mean concentrations of Mn, La, Ce, and Ba were comparable to their reference values. This result indicates that Mn, La, Ce, and Ba were derived mainly from natural sources, while the other elements were influenced by anthropogenic emissions. Skewness values also showed that only Mn, La, Ce, and Ba approached a normal distribution, while the other metal elements were positively skewed towards lower concentrations.

3.2 Correlation coefficient analysis

Table 2 lists the Spearman correlation coefficients among the 14 metal elements measured in road sediment ($n=35$) from Guangzhou. The PGEs (Pt, Pd, and Rh) show significant linear positive correlations, which could indicate a common source. Significant positive correlations are also found between Mo and Pt, Pd, Rh, Mn, Cu, and Pb. La and Ce show a very strong positive correlation ($r=0.982$), which likely reflects their similar geochemical nature. However, they each show a weak correlation with Pt, Pd, Rh, and Mn. Though Pb and Zn have similar geochemical properties, they show a very weak correlation, probably reflecting the influence of traffic and industrial activities.

Table 1 Descriptive statistics for PGEs and other heavy metal contaminants in road sediment from Guangzhou

Element ^a	Minimum	Maximum	Mean	Median	SD	CV	Skewness	Background ^b
Pt	12.35 (18.0)	152.8 (249)	68.24	62.82	40.53	0.59	0.42	0.50
Pd	9.69 (13.2)	262.8 (330)	93.15	72.34	70.17	0.75	0.66	0.65
Rh	4.09 (184)	64.35 (3086)	23.85	18.86	15.28	0.64	1.04	0.017
Cr	80.96 (1.00)	305.4 (3.92)	147.5	133.2	50.06	0.34	1.54	65
Mn	527.6 (0.73)	920.7 (1.29)	712.3	695.2	108.4	0.15	0.17	600
Ni	20.32 (0.63)	84.13 (2.68)	47.24	43.07	14.62	0.31	0.75	26
Cu	114.8 (3.75)	290.5 (10.5)	177.5	175.3	47.25	0.27	0.88	24
Zn	466.5 (5.42)	4,086 (54.2)	1,254	911.5	1,090	0.87	2.03	68
La	30.08 (0.61)	69.87 (1.50)	47.50	48.94	10.30	0.22	0.12	38
Ce	59.35 (0.63)	150.2 (1.71)	96.62	97.85	22.97	0.24	0.34	72
Mo	2.97 (2.85)	10.33 (10.2)	4.91	4.82	1.46	0.30	1.93	0.8
Cd	1.67 (14.22)	6.74 (64.6)	3.00	2.73	1.16	0.39	1.72	0.09
Pb	71.67 (2.64)	501.3 (19.5)	198.1	192.1	79.49	0.40	2.22	23
Ba	479 (0.74)	792.5(1.44)	619.0	605.0	89.0	0.14	0.33	500
Sc	12.2	15.3	13.5	13.5	0.8	0.06	0.26	11.1

Data in parentheses are the enrichment factor (EF); $EF(i) = [C(i)/C(Sc)]_{\text{sample}} / [C(i)/C(Sc)]_{\text{reference}}$; see the text for details

^a The unit of measurement for Pt, Pd, and Rh concentrations is ng g^{-1} ; for all other elements, it is $\mu\text{g g}^{-1}$.

^b Chi and Yan (2007)

Ba and Mn are generally poorly correlated with the other metal elements, possibly reflecting a different source from the other metals.

3.3 Principal component analysis

Principal component analysis was used to assist in the identification of sources of heavy metals in road sediment by applying VARIMAX rotation with Kaiser normalization

(see Section 2.4). By extracting the eigenvalues and eigenvectors from the correlation matrix, we calculated the number of significant factors and the proportion of variance explained by each factor. Table 3 shows the results of the factor loadings with a VARIMAX rotation, as well as initial eigenvalues and communalities. These data indicate that the elemental composition of road sediment is dominated by five PCs (PC1–PC5) with loadings of 27.50, 19.57, 13.43, 9.08, and 8.15 %, respectively.

Table 2 Spearman correlation matrix for platinum-group elements and other trace metal concentrations

	Pt	Pd	Rh	Cr	Mn	Ni	Cu	Zn	La	Ce	Mo	Cd	Pb	Ba
Pt	1.000													
Pd	0.839**	1.000												
Rh	0.844**	0.808**	1.000											
Cr	0.266	0.307	0.257	1.000										
Mn	0.187	0.224	0.234	0.397*	1.000									
Ni	-0.049	-0.114	0.100	0.227	-0.137	1.000								
Cu	0.109	-0.045	0.170	0.330	-0.013	0.515**	1.000							
Zn	0.117	0.051	0.322	0.118	0.154	0.397*	0.120	1.000						
La	0.296	0.260	0.248	0.144	0.319	-0.147	0.040	-0.136	1.000					
Ce	0.359	0.298	0.317	0.147	0.352	-0.197	0.047	-0.088	0.982**	1.000				
Mo	0.435*	0.399*	0.606**	0.344	0.397*	0.101	0.413*	0.507**	0.161	0.237	1.000			
Cd	0.139	0.231	0.183	0.340	0.049	0.228	0.375	0.328	-0.137	-0.090	0.321	1.000		
Pb	0.184	0.347	0.273	0.347	0.234	-0.134	0.067	0.145	0.366	0.360	0.460*	0.478*	1.000	
Ba	0.119	0.181	0.275	0.227	0.132	0.251	0.405*	0.123	-0.126	-0.121	0.295	0.310	0.310	1.000

* $P < 0.05$ (two-tailed)

** $P < 0.01$ (two-tailed)

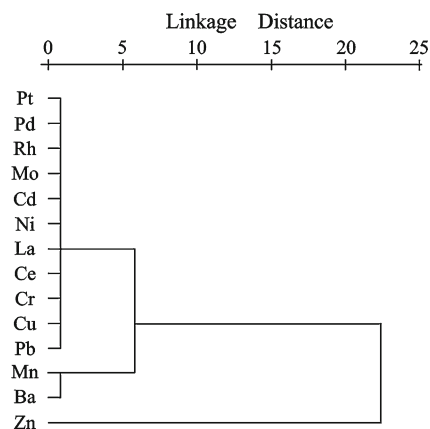
Table 3 Rotated component matrix for road sediment data in Guangzhou (PCA loadings >0.4 are shown in italics)

Element	Component					Communities
	1	2	3	4	5	
Pt	<i>0.94</i>	0.14	0.07	0.01	-0.04	0.90
Pd	<i>0.93</i>	0.10	-0.01	0.09	0.14	0.91
Rh	<i>0.91</i>	0.01	0.14	0.20	-0.05	0.89
Cr	0.12	0.21	<i>0.76</i>	0.03	0.22	0.69
Mn	0.08	0.31	0.11	<i>0.78</i>	-0.13	0.75
Ni	-0.09	<i>-0.48</i>	<i>0.74</i>	0.01	-0.17	0.81
Cu	-0.03	-0.03	<i>0.78</i>	-0.02	0.08	0.61
Zn	0.13	<i>-0.78</i>	0.12	0.02	-0.06	0.64
La	0.22	<i>0.87</i>	0.13	0.10	0.03	0.84
Ce	0.30	<i>0.87</i>	0.12	0.06	0.01	0.86
Mo	0.30	0.10	<i>0.71</i>	0.26	0.03	0.67
Cd	0.12	<i>-0.47</i>	0.26	0.02	<i>0.61</i>	0.68
Pb	-0.04	0.25	0.04	0.06	<i>0.89</i>	0.86
Ba	0.17	-0.18	0.03	<i>0.81</i>	0.21	0.76
Initial Eigenvalues	3.85	2.74	1.88	1.27	1.14	
Percent of variance	27.50	19.57	13.43	9.08	8.15	
Cumulative percent	27.50	47.07	60.50	69.58	77.73	

Collectively, these PCs account for 77.73 % of the total variance. Based on the loading distributions, Pt, Pd, and Rh are strongly associated with PC1, but very small loadings are found for the other PCs. This suggests that the distributions of Pt, Pd, and Rh are controlled by one major factor (i.e., one source). PC2 is dominated by La, Ce, Zn, Cd, and Ni, which account for 19.57 % of the total variance. With respect to PC2, the Cd, Ni, and Zn loadings are negative (-0.47, -0.48, and -0.78, respectively) and not as high as the loadings of the other elements of this group. This finding suggests a quasi-independent behavior within the group, and a different source. Cr, Ni, Cu, and Mo are closely associated with PC3; Ba and Mn with PC4; and Pb and Cd with PC5.

3.4 Cluster analysis

Cluster analysis was applied to standardized bulk concentration data using Ward's method (Han et al. 2006) with Euclidian distances as the criterion for forming clusters. The CA results for the heavy metals are shown in Fig. 2 as a dendrogram. Three clusters were identified: (1) Mo–Cd–Rh–Ni–La–Pt–Pd–Ce–Cr–Cu–Pb; (2) Mn–Ba; and (3) Zn. This finding is in agreement with the PCA results as a whole (Section 3.3). Clusters 1 and 2 join together at a relatively high level, possibly implying a common source.

**Fig. 2** Dendrogram derived using Ward's method of hierarchical cluster analysis for 14 different elements

3.5 Source identification

It has been well documented that the elemental composition of road sediment can reflect mixed origins, including geogenic and a wide range of anthropogenic sources (e.g., de Miguel et al. 1997; Duzgoren-Aydin et al. 2006b). Therefore, it is difficult to ascribe a specific source to heavy metals in urban environments. In this study, multivariate statistical analysis was used to identify the sources of platinum-group and other traffic-related heavy metals in road sediment from Guangzhou.

Compared with background values measured in soil, the extremely elevated concentrations of Pt, Pd, Rh, Zn, Cd, Pb, Cu, Cr, Mo, and Ni in Guangzhou road sediment suggest anthropogenic sources. Other elemental concentrations (La, Ce, Mn, and Ba) were slightly higher than, or approximately equal to, their corresponding background values in most of the samples, likely indicating a geogenic origin. Values of skewness and coefficients of variation (CV) further suggested these origins. The correlation coefficient analysis suggested that Pt, Pd, and Rh have a common source, while La and Ce have a different common source. PCA and CA results were consistent with these interpretations. Based on all of the analyses carried out, four main sources (with corresponding cluster elements) could be identified: (1) Pt, Pd, and Rh represented traffic sources; (2) La, Ce, Mn, and Ba were derived mainly from natural sources, although La and Ce also had traffic sources, and Mn and Ba also had minor industrial sources; (3) Cr, Ni, Cu, Mo, Cd, and Pb had mixed sources of traffic and industry; and (4) Zn originated mainly from industrial sources.

The first group of elements (Pt, Pd, and Rh), which have the highest enrichment factors among the examined elements in comparison with reference values, show strong positive correlations in the PCA and correlation coefficient analysis and are classified together in the CA. These three metals are the active catalytic materials in vehicle exhaust

converters and have consequently become concentrated in urban road sediment since their introduction (Gómez et al. 2001; Leopold et al. 2008; Prichard et al. 2009). In Guangzhou, higher concentrations of these elements were found in samples collected from high-traffic sites, indicating the elements originated from traffic sources (i.e., from vehicle exhaust catalysts).

Descriptive statistical data indicate that the second group of elements identified in the analyses (La, Ce, Mn, and Ba) was derived mainly from natural sources. Based on the correlation analysis, PCA and CA, this group can be further subdivided into two sub-clusters: (1) La and Ce are significantly correlated, and (2) Mn and Ba are well correlated, although they show a weaker correlation in the correlation coefficient analysis. The maximum concentrations of La, Ce, Mn, and Ba are 1.5–2 times greater than the corresponding background values of soil, indicating some anthropogenic influence. La and Ce are moderately correlated with Pt, Pd, and Rh in the correlation coefficient analysis and PCA, and are classified together with PGEs in the CA, suggesting a traffic source. Mn and Ba are strongly correlated in the PCA and are clearly separated from the other metals in CA, suggesting an anthropogenic source other than traffic (e.g., rubber production, lubricating oil additives, fuel synthesis, fuel combustion, phosphate fertilisers, and sewage sludge; Sutherland 2000).

The third group of elements (Cr, Ni, Cu, Mo, Cd, and Pb) is significantly correlated in the correlation coefficient analysis and is classified together with PGEs in the CA, indicating a traffic source. However, this group is associated with two principal components (PC3 for Cr, Ni, Cu, and Mo; PC5 for Cd and Pb) and is separate from PGEs in the PCA. This result suggests that the third group of elements was not derived from traffic sources alone. In fact, Cr, Ni, Cu, Cd, and Pb may originate from various industries besides traffic. For example, other potential sources of Cd include lubricating oil, diesel oil, tyres, phosphate fertilisers, insecticides, electroplating, pigments, batteries, coal and oil combustion, non-ferrous metal production, refuse incineration, and iron and steel manufacturing. In addition to diesel fuel and vehicle exhaust, Ni can originate from lubricating oil, metal plating, brushing wear, brake lining wear, phosphate fertilisers, and storage batteries (Sutherland 2000). Thus, the third group of elements identified in the analyses is suggested to have originated from combined industrial and traffic sources.

The fourth group (Zn) is separate from the other elements in the CA, suggesting a distinct source. The Zn in Guangzhou road sediment shows the highest mean concentration, and largest CV and skewness. In addition, Zn is negatively correlated with La and Ce in the correlation coefficient analysis and the PCA. This finding suggests anthropogenic sources. Zn is typically a traffic-related element that may originate from fossil fuels, combustion exhaust, brake

lining, and rubber tyres (Councell et al. 2004). However, traffic does not appear to be the main source of Zn in this study, and may have originated from other sources such as grease, batteries, galvanising, plating, air-conditioning ducts, pesticides, phosphate fertilisers, transmission fluid, asphalt paving, concrete, smelting operations, incineration, and wood combustion (Sutherland 2000). For example, a significant amount of asphalt was used as paving for the 2010 Guangzhou Asian games, which could have contributed to the significantly elevated levels of Zn measured in road sediment in the present study.

3.6 Enrichment factor analysis

EFs of the different elements (normalized against Sc) are shown in Fig. 3. The three PGEs, especially Rh, have unusually high EFs, suggesting anthropogenic sources. In contrast, La, Ce, Mn, and Ba have EFs of <2 in all road sediment samples, confirming that their origin was mainly from natural sources. Other elements (Cr, Ni, Cu, Zn, Mo, Cd, and Pb) have EFs indicating low deficiency to extremely high enrichment, but maximum EFs >3 suggest some anthropogenic influence (Han et al. 2006).

The mean EFs ranked in decreasing order are as follows: Rh>Pd>Pt>Cd>Zn>Pb>Cu>Mo>Cr>Ni>Ce>La>Ba>Mn. This order can be interpreted to indicate the relative levels of contamination of each element in road sediment from Guangzhou. Pt, Pd, and Rh have mean EFs above 40, suggesting extremely high levels of contamination; Cr, Mn, Ni, La, Ce, and Ba have mean EFs of <2, representing depletion to minimal levels of contamination; and Cd, Zn, Pb, Cu, and Mo have mean EFs between 5 and 40, indicating significant to very high contamination. Maximum EFs may also reflect the degree to which each metal is affected by local

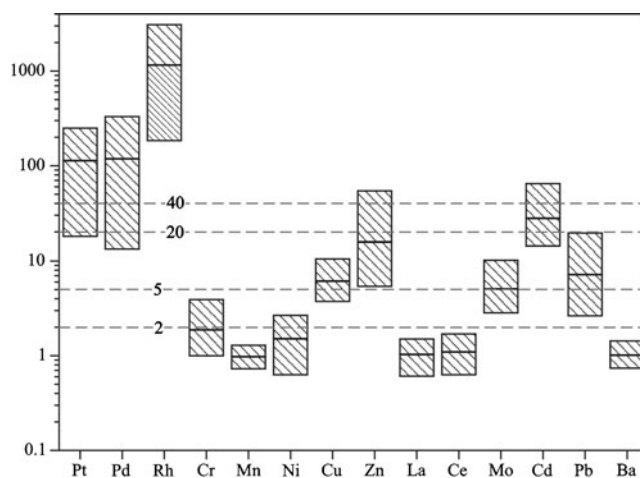


Fig. 3 Boxplot of enrichment factors for traffic-related heavy metals in road sediment from Guangzhou (all EFs are log normalized; the height of each box represents the range; the thick line inside each box represents the mean)

pollution. The maximum EFs of Pt, Pd, Rh, Cd, and Zn are above 50, suggesting extremely high contamination of local road sediment; the maximum EF of Pb is 19.5, equating to very high contamination; Cu and Mo have maximum EFs of 10.5 and 10.2, respectively, indicating significant contamination. The EFs of La, Ce, Mn, and Ba are very low (0.61–1.50, 0.63–1.71, 0.73–1.29, and 0.73–1.77, respectively), reflecting minimal levels of contamination. These observations show that EFs can be an effective tool for evaluating the contribution of anthropogenic and natural sources to heavy metal contamination of road sediment.

4 Conclusions

This study analyzed the concentrations and sources of the platinum-group and other traffic-related heavy metals, including Pt, Pd, Rh, Cr, Mn, Ni, Cu, Zn, La, Ce, Mo, Cd, Pb, and Ba, in road sediment samples collected from Guangzhou. The mean concentrations of these heavy metals are higher than corresponding background values measured in soils in China. This was particularly true for Pt, Pd, Rh, Cd, and Zn, for which we obtained significantly higher concentrations than background values.

Based on coefficients of variation and skewness values, and a comparison between concentrations measured in road sediment and soil, the heavy metals were classified into two main groups according to their sources: geogenic and anthropogenic. PCA, CA, and correlation coefficient analysis enabled four further groups to be identified. First, Pt, Pd, and Rh were derived from traffic sources. Second, La, Ce, Mn, and Ba were derived mainly from natural sources, although La and Ce were also influenced by other traffic sources, and Mn and Ba were influenced by minor industrial sources. Third, Cr, Ni, Cu, Mo, Cd, and Pb showed mixed traffic and industry sources. Fourth, Zn originated mainly from industrial sources. EF analysis supported this source identification and further indicated that contamination of road sediment in Guangzhou is extremely high for Pt, Pd, and Rh; moderate to very high for Cd, Zn, Pb, Cu, and Mo; and minimal for Cr, Ni, La, Ce, Mn, and Ba.

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