Multivariate statistical analysis of heavy metals in foliage dust near pedestrian bridges in Guangzhou, South China in 2009

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Abstract The heavy metal content of particulate matter was investigated in the city of Guangzhou in southern China. Samples of urban foliage near 36 pedestrian bridges were analyzed to determine their Zn, Pb, Cu, Cr, V, Ni, and Co contents after digestion in a mixture of strong acids composed of HNO₃, HCl, HF, and HClO₄. The results revealed a severe heavy metal pollution compared with the background levels in Chinese soils, except for Co and V. The mean concentrations of Zn (1,024 mg kg⁻¹), Pb (233 mg kg⁻¹), Cu (203 mg kg⁻¹), Cr (118 mg kg⁻¹), Ni (41.4 mg kg⁻¹), and Co (11.3 mg kg⁻¹) in urban dust were higher than the reference levels, and were highest in samples located near high-traffic areas. Multivariate statistical methods (correlation analysis, principal-components analysis, and clustering analysis) were used to identify the possible sources of the metals. Three main pollutant sources are assigned: Zn, Cu and Ni levels were strongly correlated and were possibly related to combustion processes and vehicles; Pb, Cr and Co were mainly derived from traffic sources, combined with soil sources; and V mainly originated from natural sources.

Keywords Dusts · Heavy metals · Particulate matter · Pedestrian Bridges · Guangzhou

Introduction

With the rapid pace of global industrialization and urbanization, particularly in megapolises, urban environmental problems, and especially the degradation of urban air quality, have become a major adverse side-effect with severe negative effects on the health of human beings and on sustainable socioeconomic development. The particulate matter generated in urban environments is believed to be a leading killer of humans, as it contains many hazardous materials such as heavy metals, acid oxides, organic matter, bacteria, and viruses. Among these particulates, the adverse effects of the size classes smaller than 2.5 μm (PM₂.₅) and 10.0 μm (PM₁₀) have been studied in detail (Alleman et al. 2010; Dongarra et al. 2010; Lim et al. 2010; Muránszky et al. 2011); however, particulates with a larger grain size, and particularly the particulates called “foliage dust” because they are frequently deposited on the surface of leaves, have received much less attention around the world. Field observations have confirmed that foliage dust provides strong clues to the characteristics of the urban atmospheric environment (Coe and Lindberg 1987; Freer-Smith et al. 1997; Bargagli 1998; Wang et al. 2009). Therefore, the heavy metal concentration in foliage dust has been used as an
indicator and pollution monitor of the urban atmospheric environment (Tomasevic et al. 2005; Simon et al. 2011). For example, Simon et al. (2011) reported that the heavy metal concentrations in foliage dust were significantly higher in an urban area of Vienna, Austria, than in a rural area of the city, and the urbanization significantly increased the heavy metal concentrations in foliage dust. Maher et al. (2008) analyzed leaves at different heights in Norwich (UK) and found that particulate Pb concentrations were highest at ~0.3 m (i.e., about the height of a small child) and at 1.5–2.0 m (head height for an adult) above ground level. Moreover, Tomasevic et al. (2005) studied the characteristics of heavy metal particles deposited on tree leaves in the urban area of Belgrade (Serbia and Montenegro), and found that the deposited particles were mainly originated from vehicle traffic and from resuspended particulate matter. In the urban area of Hangzhou (China), Lu et al. (2008) noted that the dust on tree leaves contained high concentrations of Pb (a mean of 150.9 mg kg\(^{-1}\)), Zn (535.9 mg kg\(^{-1}\)), Cu (63.7 mg kg\(^{-1}\)), and Cd (2.62 mg kg\(^{-1}\)). Qiu et al. (2009) studied the foliage dust on urban leaf surfaces in Huizhou, southern China, and found that the heavy metal contents were high, particularly for Pb and Cd, which ranged from 434.0 to 512.0 mg kg\(^{-1}\) and 6.2 to 12.8 mg kg\(^{-1}\), respectively.

Guangzhou, the capital of Guangdong Province and part of the Pearl River Delta region, is one of China’s largest industrial centers and fastest expanding cities (Duzgoren-Aydin 2007). Its rapid economic development has brought great prosperity to the region, but has also given rise to a wide variety of environmental problems, particularly in terms of traffic jams and air pollution. When Guangzhou was awarded the right to host the 2010 Asian Games, the local environmental protection authority invested 600 million RMB to improve the city’s air quality. The effects of air pollution are currently a serious concern to the local government, to citizens, and to tourists. Moreover, because of the city’s well-developed traffic system, dozens of roads criss-cross the urban region. To help pedestrians cross these busy roads conveniently and safely, hundreds of pedestrian bridges have been installed. The pedestrian bridges are located at a height of about 5 m, and Bougainvillea spectabilis Willd has been planted alongside the bridges. As a result, this vegetation can be used as a natural collector of atmospheric particulates.

The aim of the present study was to determine the levels of seven heavy metals (Pb, Zn, Cu, Ni, Co, Cr, and V) in the urban atmosphere of Guangzhou using dust deposited on the leaf surfaces as a proxy for these levels. The results can provide a baseline for use in future environmental impact assessments and to guide pollution mitigation targets.

Materials and methods

Study area

Guangzhou is adjacent to the estuary of the Pearl River, in the southern part of China. Situated in a subtropical monsoon climate zone, it has a mild climate with a long summer and a short winter, with distinct wet and dry seasons. The mean annual temperature ranges from 20.6 to 22.5 °C, and the annual total rainfall averages approximately 2,388 mm. The winters are dry and cold, with a prevailing north wind; the summer is wet and hot, with a prevailing south wind.

The study area extends from 22°26′ to 23°56′N and from 112°57′ to 114°03′E, covering an area of more than 3,800 km\(^2\). To support a population of more than 10.33 million, the city has a well-developed transport system that includes two highways, four major north–south roads, eight major east–west roads, and hundreds of minor roads. At the end of 2009, more than 1.34 million vehicles were in use in the city. Guangzhou’s industry is scattered in and around the urban area, and the goods and services sector dominates the economy (63 % of the total economic output).

Sampling

Previous studies have shown that leaves trap particulate matter only temporarily. When precipitation is greater than 5 mm or the wind speed in greater than 17 m/s, these particulates are typically removed from the leaves (Zhao et al. 2002). Therefore, all the samples were collected in the present study from September to October in 2009, during the dry winter months. During this period, the wind speed was typically much lower than 17 m/s, and only a few precipitation events were recorded. Therefore, this was a suitable period for sample collection.

A total of 36 pedestrian bridges were chosen at different locations within the urban area of Guangzhou (Fig. 1). To obtain samples, 100–150 leaves were picked from the top part of braches above the sidewalk on each side of bridge. Every sample consisted of about 200 g of leaves. The leaves were stored in glass petri dishes during transport to prevent the loss of dust. The leaves were oven-dried at 35 °C for 3 days, and then weighed. The dust on the leaf surface was collected using a plastic brush. A different brush was used for the leaves collected at each location. Samples from each site were bulked to produce a single composite sample before analysis.

Heavy metal analysis

Each ca 0.02 g dried dust was transferred into a Teflon beaker (50 mL) and then was digested using a mixture of
strong acids composed of 1 mL HNO₃ (15.9 M), 3 mL HCl (12.1 M), 4 mL HF (28.9 M), and 2 mL HClO₄ (11.7 M). The sample was heated on a temperature-programmed hot plate for 2 h at 120 °C with the beaker covered, and then was heated to 160 °C for 10 h, until all of the samples were digested. The beaker was then uncovered and the sample was heated to 180 °C until completely dry. Afterwards, the residues were extracted with 10 ml 0.8 M high-purity HNO₃ and kept in a refrigerator prior to analysis. The heavy metal concentrations of the foliage dusts were determined using an inductively coupled plasma-optical emission spectrometer (ULTIMA 2, manufactured by HORIBA Jobin–Yvon Company, Pairs, France) at Xi’an Institute of Earth Environment, Chinese Academy of Sciences (CSA). Blanks, quality control standard samples (ESS-3, environmental soil) and duplicated samples were simultaneously performed as quality control, with standard reference materials (ESS-3) giving recoveries more than 85 % for all these trace elements according to certified values. In the measurement, the LODs of referred heavy metal are as follows: Co-0.76, Cr-0.28, Cu-0.09, Ni-1.07, Pb-10.3, V-0.55 and Zn-0.16 µg/L. On average, the analytical precision, measured as relative standard deviation (RSD), was routinely between 3 and 5 % for all analyzed elements.

Statistical analyses

The concentrations were analyzed using version 19.0 of the SPSS software for Windows (SPSS Inc., Chicago, IL, USA). Correlation matrices were used to identify the relationships among the seven elements (Han et al. 2006; Lu et al. 2010). In this analysis, Pearson’s product-moment correlation coefficient (r) was used. Principal-components analysis (PCA) were also used to group the heavy metals and infer their hypothetical source (Han et al. 2006; Tokaloğlu and Kartal 2006; Meza-Figueroa et al. 2007). The components of the PCA were transformed using a varimax rotation with Kaiser normalization after the analysis. Cluster analysis was applied to identify different geochemical groups by clustering the samples with a similar heavy metal content (Han et al. 2006; Lu et al. 2010). Cluster analysis was performed according to Ward’s method (Han et al. 2006). The results were displayed as a dendrogram created using hierarchical clustering, and values of the distances between clusters (the squared Euclidean distance) were presented.

Results and discussion

Heavy metal concentrations

Table 1 summarizes the heavy metal concentrations in the urban dust collected in Guangzhou, and presents the mean values for Chinese soils (CNEMC 1990) and local soils in the Pearl River Delta (Wong et al. 2002), which are used as the reference values for acceptable levels in China. The mean concentrations were 1,024 mg kg⁻¹ for Zn, 233 mg kg⁻¹ for Pb, 203 mg kg⁻¹ for Cu, 118 mg kg⁻¹ for Cr, 41.9 mg kg⁻¹ for V, 41.4 mg kg⁻¹ for Ni, and 11.3 mg kg⁻¹ for Co. Data as presented exhibit a considerable variations between the maximum and minimum values: Zn (2,058–355 mg kg⁻¹), Pb (504–125 mg kg⁻¹),...
Cu (469–74.8 mg kg\(^{-1}\)), Cr (266–43.1 mg kg\(^{-1}\)), V (62.9–28.2 mg kg\(^{-1}\)), Ni (65.5–19.6 mg kg\(^{-1}\)) and Co (20.4–8.3 mg kg\(^{-1}\)). Compared with the reference values of Chinese soils (Table 1), the mean concentrations of Zn, Pb, and Cu in the samples are conspicuously higher by factors of 13.8, 9.0, and 9.0. The mean concentrations of Cr and Ni are also slightly higher by factors of 1.9 and 1.5, respectively. In the meantime, the mean concentration of Co is comparable with the reference value of Chinese soil, while that of V is considerably low.

Correlation analysis

Table 2 summarizes the Pearson’s correlation coefficients (\(r\)) for the heavy metals, where all element–element pairs are positively correlated. The statistically significant pairs (\(P < 0.01\)) are outlined. Zn is significantly correlated with Cu (\(r = 0.88\)), Ni (\(r = 0.63\)), Pb (\(r = 0.53\)) and Co (\(r = 0.47\)). Pb is correlated with Cr (\(r = 0.43\)), while Ni is correlated with Cu (\(r = 0.67\)), Cr (\(r = 0.43\)) and Co (\(r = 0.41\)). Both Cu and Cr are correlated with Co with \(r\) values of 0.44 and 0.41, respectively. On the contrary, V exhibits weak (\(r \leq 0.3\)) and nonsignificant correlations with all other metals.

Principal-components analysis

Because of the complexity of the correlation results, it was necessary to perform additional analysis to group the heavy metals and infer their sources. PCA has been successfully
used to identify the sources of pollutants (Han et al. 2006; Tokaloğlu and Kartal 2006; Meza-Figueruela et al. 2007; Lu et al. 2010). By extracting the eigenvalues and eigenvectors from the correlation matrix, it was able to determine the number of significant principal components and the percentage of the total variance they explained (Table 3).

Three statistically significant components that together explained about 77% of the total variance were obtained. The first two eigenvalues (both $>1$) explained $\approx 66 \%$ of the total variance, indicating that they are the most important factors. The first factor explained 48.4% of the total variance and had the greatest weights for Cu, Zn, and Ni. Factor two had the greatest weights for Cr, Pb, and Co, and accounted for 17.5% of the total variance. The third factor (eigenvalue = 0.77) explained about 11% of the total variance, and had the strongest weight (0.94) for V. Figure 2 presents a 3-D plot of the three PCA loadings, which clearly reveals these relationships among the seven heavy metals.

Cluster analysis

Before cluster analysis, the values were standardized using $z$-scores; then the Euclidean distances among the values for the heavy metals were calculated. Finally, hierarchical clustering were performed using Ward’s method. Figure 3 shows the results as a dendrogram. The cluster has three overall subgroups: the first contains Cu, Zn, and Ni; the second contains Cr, Pb, and Co; and the third only includes V. The clustering confirmed the results of the PCA.

Source identification

The use of multivariate statistical techniques has proven to be an effective tool for extracting information on heavy metals in urban dust (Han et al. 2006; Tokaloğlu and Kartal 2006; Lu et al. 2010), such as the Principal component analysis (PCA). PCA has been widely used to identify the sources of pollutants and can effectively reduce the number of variables and thereby facilitate analysis of the relationships among the observed variables (Tokaloğlu and Kartal 2006). In general, significant correlations between pairs of heavy metals suggest a common or combined origin, whereas weak correlations indicate different origins.

Table 3 and Figs. 2 and 3 suggest that the seven heavy metals could be classified into the same three categories: Group 1 (Zn, Cu, and Ni), Group 2 (Pb, Cr, and Co), and Group 3 (V). These results indicated that Zn, Cu, and Ni probably have a mixed anthropogenic sources-including combustion processes and vehicles. Generally speaking, Zn, Cu and Ni are associated with combustion processes, for example, the combustion of coal usually emits high amounts of all three metals (Yang and Cheng 2002; Wang et al. 2008), the burning of other fossil fuels such as oil produces emissions that contain large amounts of Ni and

| Element | Principal component | Communalities |
|---------|---------------------|---------------|
|         | 1       | 2       | 3       |             |
| Co      | 0.45    | 0.46    | 0.32    | 0.52        |
| Cr      | 0.14    | 0.93    | 0.03    | 0.89        |
| Cu      | 0.95    | 0.07    | 0.05    | 0.92        |
| Ni      | 0.73    | 0.39    | -0.08   | 0.70        |
| Pb      | 0.31    | 0.54    | 0.44    | 0.58        |
| V       | -0.03   | 0.08    | 0.94    | 0.90        |
| Zn      | 0.92    | 0.20    | 0.11    | 0.89        |
| Initial eigenvalues | 3.39 | 1.22    | 0.77    |             |
| Variance (%) | 48.44 | 17.48   | 11.05   |             |
| Cumulative variance (%) | 48.44 | 65.92   | 76.97   |             |

Fig. 2 PCA loadings for the three principal components from the PCA (PC1 vs. PC2 vs. PC3) for the seven heavy metal elements. Details are shown in Table 3

Fig. 3 Hierarchical dendrogram for the seven elements obtained using Ward’s clustering method

Table 3 Results of the PCA for the heavy metal concentrations of the foliage dusts collected in Guangzhou after varimax rotation with Kaiser normalization
Cu (Yang and Cheng 2002), and waste incineration and metal smelting produce emissions containing high levels of Ni and Cu (Yang and Cheng 2002). Compared with the mean values in Chinese soils (Table 1), the mean concentrations of Zn and Cu are conspicuously higher, while Ni is slightly enriched. In this study, all the samples were collected at a height of 5–6 m above major roads surrounded by high-rise residential and commercial buildings, and there was no incineration of municipal refuse and few factories used to refine molten metal upwind of these sites. On this basis, it could hypothesize that the Group 1 metals were also mainly derived from vehicle exhaust emissions, as well as lubricating oil and grease. Because Zn, Cu, and Ni are widely used in tires and vehicle body parts, the higher wear rates that result from the high temperatures of subtropical Guangzhou may contribute to high Zn, Cu, and Ni contents in the foliage dust (Duzgoren-Aydin et al. 2006). The exhaust gases released from the restaurant industry and from residential areas surrounding the study area would have been another important source, since the local government has promoted the use of liquefied petroleum gas (LPG) for heating and cooking since 2003, largely eliminating the “black smoke” phenomenon that resulted from using coal for these purposes. However, vehicle exhaust emissions may still contain high contents of Zn and Cu. In addition, the waste gases emitted by families during cooking must not be neglected during management of the urban air environment, because coal remains a popular fuel due to its low cost.

The metals in Group 2 (Pb, Cr, and Co) were significantly correlated. The mean concentration of the Co was close to the Chinese soil reference value (Table 1), so its source is likely to be mainly from local surface soils. The mean concentration of the Cr was much higher than the mean value in Chinese soils, and its source appears to be associated with the chrome plating of some vehicle parts (Christoforidis and Stamatis 2009). The mean concentration of Pb was much higher than the background value in Chinese soil (Table 1). Many studies have confirmed that Pb is mainly produced by vehicle exhaust emissions, and it is a signature element for the pollution caused by traffic (Yang and Cheng 2002; Han et al. 2006; Lu et al. 2010). In a word, the metals in Group 2 mainly come from vehicle sources, combined with soil sources as well for Co.

Group 3 includes only V, which showed no significant correlation with any other element, indicating that it has a different source. The concentration of V was relatively consistent (see the low standard deviation and CV value in Table 1) despite significant differences in their surrounding environmental conditions. This suggests that V is likely derived from natural sources (Duzgoren-Aydin et al. 2006).

Conclusions

The concentrations and sources of the heavy metals Zn, Pb, Cu, Cr, Ni, V, and Co in foliage dusts collected near pedestrian bridges in Guangzhou have been studied in this work. The accumulation of these metals in the foliage dust is obvious, with mean concentrations significantly higher than the background values in Chinese soil for all metals except V and Co. Based on multivariate statistical analyses, the heavy metals were classified into three main groups according to their sources: (1) Zn, Cu, and Ni appear to have resulted from combustion processes and vehicles; (2) Pb, Cr, and Co appear to be produced by vehicle traffic, combined with soil sources; and (3) V, which was not significantly correlated with any other metal, probably had a natural source, possibly local soils.

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