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Characteristics and Sources of Metals in TSP and PM_{2.5} in an Urban Forest Park at Guangzhou

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Abstract: Urban forest parks play important roles in improving environments, protecting biodiversity and even public welfare. Aerosols, including total suspended particles (TSP) and particulate matter with aerodynamic diameter less than 2.5 µm (PM_{2.5}), were simultaneously collected in an urban forest park (Dafushan) at Guangzhou, southern China, from January 2012 to December 2013. The concentrations of 12 metals (Al, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, and Zn) in both TSP and PM_{2.5} were quantified using an inductively coupled plasma-mass spectrometer. The origins and possible sources of the studied metals in the PM_{2.5} and TSP were evaluated using the crustal enrichment factors and the principal component analysis, respectively. The results showed that Dafushan urban forest park was polluted by PM_{2.5} rather than by TSP. The PM_{2.5} and TSP in the forest park exhibited seasonal patterns with significantly higher contents in the dry season compared with the

rainy season. The metals Al, Zn, Pb were the most abundant, while Hg was the lowest metals in the aerosols. The ratios of $PM_{2.5}$ /TSP ratio indicated that the metals were predominant in the finer particles ($PM_{2.5}$). The crustal enrichment factors indicated that Cd, Cu, Mo, Pb, Se and Zn in the aerosols originated from anthropogenic sources, while Al and Mn were mainly of crustal origin. The principal component analysis implied that industrial activities, traffic-related emissions, and soil dust were the main possible sources of the metals in both $PM_{2.5}$ and TSP in Dafushan forest park.

Keywords: $PM_{2.5}$; TSP; metals; source identification; urban forest park

1. Introduction

Total suspended particles (TSP) and especially particulate matter with aerodynamic diameter less than $2.5\ \mu\text{m}$ ($PM_{2.5}$) are frequently considered as atmospheric pollutants due to their ability to bind to toxic substances and hazardous matter. Numerous studies have confirmed the close relationships between the high concentrations of TSP, $PM_{2.5}$ and an increased risk of respiratory symptoms, cancer and even mortality rates [1–4]. Besides their adverse effects on visibility [5], TSP and $PM_{2.5}$ have been found to be the carriers of pathogenic bacteria that lead to fatal diseases [6] and toxic metals that result in human dysfunction and various diseases [4,7,8]. Metals in particulate matter (PM) usually have both anthropogenic and natural origins. Anthropogenic sources (e.g., industrial activities, waste incineration, fossil fuel burning [4,9–11], traffic emissions [12,13]), and natural sources (e.g., crustal minerals, forest fires and oceans) were the principal contributors to metals in the ambient air [14–16].

In recent years, China has undergone severe haze pollution due to the intensive emissions of air pollutants coupled with the rapid industrialization and urbanization [4,11]. A very high level of $PM_{2.5}$ with an annual average concentration over $90\ \mu\text{g}\cdot\text{m}^{-3}$ was recently estimated in the Pearl River Delta of southern China [17,18]. The toxic metals in aerosols originating from the intensive anthropogenic activities were reported at concentrations far higher than their natural background levels in many regions of China, especially in the city clusters such as the Yangtze River Delta, Beijing-Tianjin Area, and the Pearl River Delta [4,18–21]. In urban areas, the spatial-seasonal variability, characterization and sources assignation of PM as well as the concentrations of pollutants in PM, have been frequently of concern in areas such as traffic and residential districts and hospitals [18–20]. The characteristics and sources of metals in aerosols at recreational areas such as urban forest parks have seldom been considered [22–24]. Knowledge of metals (*i.e.*, their characteristics and sources) in forest park aerosols is of great significance for the air quality and the public health of urban inhabitants.

Guangzhou is a highly industrialized and urbanized metropolitan located in the Pearl River Delta of southern China. It has a total area of greater than $7400\ \text{km}^2$ and a population of more than 13 million people [25]. The reported daily average level of $PM_{2.5}$ ($107.5 \pm 34.0\ \mu\text{g}\cdot\text{m}^{-3}$) in the downtown area was considerably higher than the national standard of $35.0\ \mu\text{g}\cdot\text{m}^{-3}$ [17]. Fortunately, for benefits such as environmental improvement, biodiversity protection, and public welfare, many urban forest parks have been built across the urban areas of southern China during the past years [23,26]. The public has become increasingly concerned about the air quality in urban forest parks. In the present study, we selected an

urban forest park in Guangzhou (Dafushan forest park) to investigate (1) the characteristics of TSP, PM_{2.5} and their metal concentrations and (2) the potential origins and sources of the studied metals. Results of this type of research are expected to be useful for the characterization and planning of emissions control of metals around the urban forest parks and to be important for the welfare of the population, especially in highly polluted areas.

2. Results and Discussion

2.1. Seasonal PM Comparison

The mean concentrations of the TSP and PM_{2.5} in Dafushan forest park were showed in Table 1. The annual TSP level was comparable to the National Ambient Air Quality Standard (NAAQS) of 120 $\mu\text{g}\cdot\text{m}^{-3}$, while the PM_{2.5} level was approximately twice as high as the NAAQS of 35 $\mu\text{g}\cdot\text{m}^{-3}$ [27]. These results implied that the urban forest park was polluted by PM_{2.5} rather than TSP. In comparison with other urban areas in Guangzhou, this urban forest park had a lower PM_{2.5} than the hospitals ($97.86 \pm 51.81 \mu\text{g}\cdot\text{m}^{-3}$) [18], the residential districts ($85.55 \pm 37.25 \mu\text{g}\cdot\text{m}^{-3}$), the roadsides ($109.70 \pm 43.95 \mu\text{g}\cdot\text{m}^{-3}$), and the industrial plants ($101.52 \pm 30.41 \mu\text{g}\cdot\text{m}^{-3}$) [28]. In addition, the PM_{2.5} in this park was also lower than that in Chongming island forest park at Shanghai ($89.2 \mu\text{g}\cdot\text{m}^{-3}$) [22], but considerably higher than that in K-pusta park of Hungary ($12.7 \mu\text{g}\cdot\text{m}^{-3}$) [29], Hohenpeissenberg forest park of Germany ($10.6 \mu\text{g}\cdot\text{m}^{-3}$) [30], and Triangle Park ($20.1 \mu\text{g}\cdot\text{m}^{-3}$) of USA [31], which implied that the finer particle concentration in Dafushan forest park at Guangzhou was relatively high.

Table 1. Statistics of the particulate matters (total suspended particles (TSP) and particulate matter with aerodynamic diameter less than 2.5 μm (PM_{2.5})) ($\mu\text{g}\cdot\text{m}^{-3}$), the PM_{2.5}/TSP ratios, and the relationship between TSP and PM_{2.5} in Dafushan forest park.

Season	PM	Values					PM _{2.5} /TSP		
		Max.	Min.	Mean	SD	CV	SD	CV	Mean
Rainy season	TSP	246.71	59.85	101.32	43.29	0.43	0.44	1.12	0.40
	PM _{2.5}	105.69	18.27	40.18	19.11	0.48			PM _{2.5} = 0.98TSP + 12.82 ($r = 0.62$)
Dry season	TSP	387.23	48.96	152.65	82.87	0.55	0.34	0.69	0.49
	PM _{2.5}	140.72	26.37	73.58	28.32	0.38			PM _{2.5} = 1.27TSP + 23.04 ($r = 0.79$)
Annual	TSP	347.23	48.96	137.41	66.34	0.46	0.51	1.17	0.43
	PM _{2.5}	140.72	18.27	62.52	33.58	0.54			PM _{2.5} = 1.05TSP + 16.57 ($r = 0.68$)

As presented in Table 1, the concentrations of TSP and PM_{2.5} were significantly higher in the dry season than in the rainy season ($p = 0.006$ and 0.023 , respectively). The significant difference in meteorological conditions between the seasons [32,33] might lead to the differences in PM concentrations. The stronger air convection activities, and more frequent and intensive precipitation in the rainy season compared with the dry season at Guangzhou facilitates the diffusion and the dilution of PM [28,33,34]. However, the prevailing wind from the north in winter could transport atmospheric pollutants from the inland area of China [28]. The lower ratio of PM_{2.5}/TSP ratio in the rainy season implied that fine particulate matter exposed to higher humidity or precipitation might be easily removed [33]. Furthermore, the PM_{2.5} was strongly related to the TSP mass (the correlation coefficient

r was 0.62, 0.79 and 0.68 for the rainy, dry season and annually, respectively, Table 1), and the correlation was stronger in the dry season compared with the rainy season.

2.2. Concentration of Metals in TSP and PM_{2.5}

The mean \pm SD of the studied metals in both the TSP and PM_{2.5} samples collected from the urban forest park were presented in Table 2. The metal concentrations in the TSP and PM_{2.5} decreased in the order of Al, Zn, Pb, Cu, Mn, Cr, Ni, Se, Mo, Cd, Co, and Hg. Aluminum, Zn and Pb were the most abundant, while Hg was the least abundant metals in both the TSP and PM_{2.5}. Except for Co, Cr, Ni and Se, metals in PM_{2.5} and TSP in the dry season were significantly higher than those in the rainy season. The different behavior of those four metals might be associated with the rainy/dry seasons. There is a consistent and large demand for electric power in the Pearl River Delta in summer, which is mainly produced by thermal power plants burning coal, leading to a higher concentration of these metals in summer compared with winter [28]. These metals (especially Se) are often the indicators of coal combustion. Notably, metals in both the PM_{2.5} and TSP exhibited statistically different seasonal patterns except for Se and Hg. The higher p -values for Se and Hg might imply that both the metals had synchronous seasonal variations.

All the studied metals in the aerosols of Dafushan forest park were present in lower concentrations than those measured at hospitals, roadsides, residential and industrial areas at Guangzhou [5,18,28]. The relatively high PM_{2.5}/TSP ratios (higher than 50%) indicated that the metals were predominant in the finer particles (PM_{2.5}) in the rainy and dry seasons [4]. Our results were consistent with the findings in the aerosols from the hospitals, roadsides, residential districts and industrial plants at Guangzhou [5,18].

Table 2. Metal concentrations (mean \pm SD) in the TSP and PM_{2.5} (ng·m⁻³) in the rainy and dry seasons. The values of p -PM_{2.5} and p -TSP values indicated the significant differences in the same metal in the PM_{2.5} and TSP, respectively, between the rainy and dry seasons.

Metals	Rainy Season			Dry Season			p -PM _{2.5}	p -TSP
	TSP	PM _{2.5}	PM _{2.5} /TSP (%)	TSP	PM _{2.5}	PM _{2.5} /TSP (%)		
Al	983.64 \pm 154.48	708.17 \pm 201.65	72.02	1121.07 \pm 268.94	860.46 \pm 188.35	76.71	0.034	0.018
Zn	685.14 \pm 92.37	575.46 \pm 61.59	83.94	732.70 \pm 120.48	636.41 \pm 104.33	86.89	0.026	0.031
Pb	77.93 \pm 36.49	71.99 \pm 33.18	92.31	124.85 \pm 41.27	117.58 \pm 37.89	94.18	0.018	0.011
Cu	27.24 \pm 12.56	21.28 \pm 10.59	78.12	62.71 \pm 17.63	57.89 \pm 16.37	92.31	0.007	0.009
Mn	21.61 \pm 16.34	15.22 \pm 16.35	70.43	46.76 \pm 28.49	38.13 \pm 24.08	81.54	0.015	0.036
Cr	18.34 \pm 6.67	17.38 \pm 6.24	94.77	14.39 \pm 5.81	12.47 \pm 4.67	86.66	0.042	0.025
Ni	12.17 \pm 6.06	10.65 \pm 2.49	87.51	7.62 \pm 3.84	6.33 \pm 1.82	83.07	0.031	0.013
Se	4.68 \pm 1.64	4.02 \pm 1.26	85.90	5.56 \pm 1.52	4.31 \pm 1.81	77.52	0.082	0.261
Mo	2.52 \pm 1.75	1.87 \pm 1.13	74.21	4.74 \pm 2.98	3.85 \pm 1.91	81.21	0.017	0.008
Cd	3.09 \pm 0.58	2.52 \pm 0.69	81.55	3.43 \pm 0.72	3.06 \pm 1.04	89.23	0.044	0.047
Co	0.99 \pm 0.42	0.72 \pm 0.27	72.73	0.82 \pm 0.35	0.55 \pm 0.23	67.07	0.013	0.029
Hg	0.02 \pm 0.02	0.01 \pm 0.02	50.00	0.03 \pm 0.02	0.02 \pm 0.01	66.67	1.588	2.863

2.3. Enrichment Factors Analysis

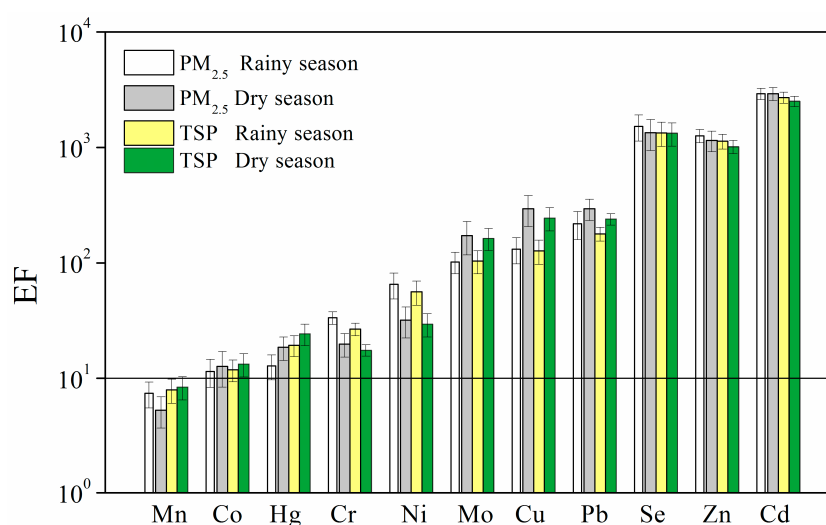
The crustal enrichment factors (EFs), defined as:

$$EF_X = \frac{(C_X/C_{REF})_{aerosol}}{(C_X/C_{REF})_{soil}}$$

could be used to distinguish the crustal and the anthropogenic origins of elements detected in the aerosols [33]. Here, C_X is the concentration of a specific element and C_{REF} is the concentration of an element known to be of crustal origin. Generally, the reference element could be Si, Al, or Fe for crustal particles in the calculation of EFs based on the crustal chemical composition provided [35]. In this study, the average upper-crust concentration of Al reported for Guangdong province [36] was selected for the evaluation of EFs. According to Cesari *et al.* [35], when the average upper-crust composition from literature data was used, an element with an EF less than 10 was likely of crustal origin, and likely of anthropogenic origin if the value was higher than 20. An element with an EF between 10 and 20 could be considered of mixed origins [35]. The enrichment factors of each element in the aerosols from Dafushan forest park between the rainy and dry seasons were presented in Figure 1.

Cadmium, Se and Zn had the highest EFs (>1000) in the PM_{2.5} and TSP samples, followed by Cu, Pb and Mo (>100) and Co, Cr, Hg and Ni (ranged from 10 to 99). Manganese had the lowest EF (<10). The metals with high EFs implied that their dominant source was anthropogenic emissions. Notably, the metals (Cd, Cu, Mo and Se) with high EFs (50–10,000) and low concentrations might imply a none-crustal origin. The relatively high concentration but considerably low EF (<10) of Mn indicated its crustal origin both in the TSP and the PM_{2.5}. The results agreed well with the metal origins in urban residential, roadside and hospital areas at Guangzhou [18,28]. The EFs did not differ significantly between the seasons, which might be due to the synchronous seasonal variation of the reference element (Al).

Figure 1. Enrichment factors of the metals in PM_{2.5} and TSP sampled in dry and rainy seasons. The ANOVA test showed there were no significant differences between the seasons.



2.4. Sources Identification Using PCA

Principal component analysis (PCA) with Varimax rotation was frequently used to determine the sources of metals in PM samples [13,35,37]. According to Henry *et al.* [38], the minimum number of

samples (N) required to obtain a statistically stable PCA analysis was $N > 30 + 0.5 \times (V + 3)$, where V is the number of species considered. In addition, the signal-to-noise ratios (S/N) of the different species should be evaluated prior to the analysis [37,38]. Further, only elements with more than 60% of values higher than the LOD should be considered [39]. The dataset used in this work satisfied these limits and all variable included in the PCA were strong (S/N greater than 2 [40]), and all the metal concentrations were higher than the LOD.

In our dataset, three components were individuated that explained more than 80% of the variance of the PM_{2.5} and TSP. The matrix of loads (after rotation) was shown in Table 3 (only loads with absolute values greater than 0.3 were listed) together with the variance explained by each component and the commonality of each species. For the PM_{2.5}, PC1 had high loading for Co, Mo, Hg, Ni, Cu, and Se, which explained 65.3% of the total variance. This factor might be associated with a mixed contribution of coal and oil combustion (Se and Ni), waste incinerators (Mo, Co, Cd, and Hg) and traffic-related emissions (Cu, Cr, and Ni) [14,16,41–44]. Thus, PC1 could be a mixed source from industrial activities and traffic-related emissions. PC2 explained 12.8% of the total variance with high loading on Pb, Se, and Cd, which represented traffic-related sources [45]. PC3 explained 7.4% of the total variance with high loading on Al and Mn, indicating a soil dust contribution [16].

Table 3. Rotated factor loading of trace metals in PM_{2.5} and TSP during sampled periods in Dafushan forest park. The principal components loading with absolute values greater than 0.3 were listed.

Variable	PM _{2.5}			TSP		
	PC1	PC2	PC3	PC1	PC2	PC3
Al			0.86	0.79	−0.48	
Cd	0.74	0.53	−0.32	0.75	0.45	
Co	0.94		−0.34	0.86		
Cr	0.58			0.78		−0.35
Cu	0.86	−0.38		0.65		0.51
Hg	0.88			0.77	−0.46	
Mn	0.46		0.63	0.96		
Mo	0.89			0.79	−0.37	
Ni	0.86			0.30		0.77
Pb	0.58	0.71		0.56	0.74	
Se	0.77	0.54		0.81	0.43	
Zn	0.75	−0.41		0.72	0.53	0.41
% of variance	65.3	12.8	7.4	58.3	14.5	10.6
Cumulative	65.3	78.1	85.5	58.3	72.8	83.4
Main sources	Industry& Traffic	Traffic	Soil dust	Industry& Soil dust	Traffic	Industry

For the TSP, the PCA results demonstrated three components accounting for 83.4% of the variance. The first component (PC1) explained approximately 58% of the total variance and was loaded with Al, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, and Se, which indicated the likely sources of metals in the TSP were waste incinerators (Cd, Co, Hg, Mo, and Se), oil combustion (Cr and Ni) and crustal origin (Al and Mn) [9,35,43,44]. Thus, this factor could be associated with a mixed contribution from industry

and soil dust origin. The second component (PC2) with high loading on Pb and Zn explained approximately 15% of the total variance and could be associated with traffic emissions. The third component (PC3) had relevant loads for Cu and Ni and explained 10.6% of the total variance. This factor could represent industrial emissions. In the present study, the PCA results showed that the used receptor model was unable to separate the sources affecting the measurement site. This was likely related to the limited number of metals used in the analysis. However, researchers that have used few metals in a PCA have still been able to identify the possible sources of these metals in aerosols [40,43].

3. Materials and Methods

3.1. Sampling Site

Dafushan urban forest park is located in southern Guangzhou, Guangdong province ($22^{\circ}57'N$ – $22^{\circ}58'N$, $113^{\circ}17'E$ – $113^{\circ}18.8'E$) (Figure 2) and was one of the venues for the 2010 Asian games. The park contains approximately 600 hm^2 of forest vegetation and attracts more than one million visitors annually. Guangzhou is characterized by a subtropical climate with a mean annual rainfall of 1700 mm distributed seasonally, with approximately 80% falling in the rainy season (from April to September) and approximately 20% in the dry season (from October to March). The meteorological data for Dafushan forest park were listed in Table 4 [26]. In the rainy season, the prevailing wind from the south brings clean air from the Pacific Ocean and South China Ocean, while in the dry season, the prevailing wind from the north brings air from the inland area of China. There are no high buildings, factories or point-sources of contamination in this park; however, there are municipal traffic, residential and commercial activities around the park.

Figure 2. Locations of Dafushan forest park in Guangzhou.

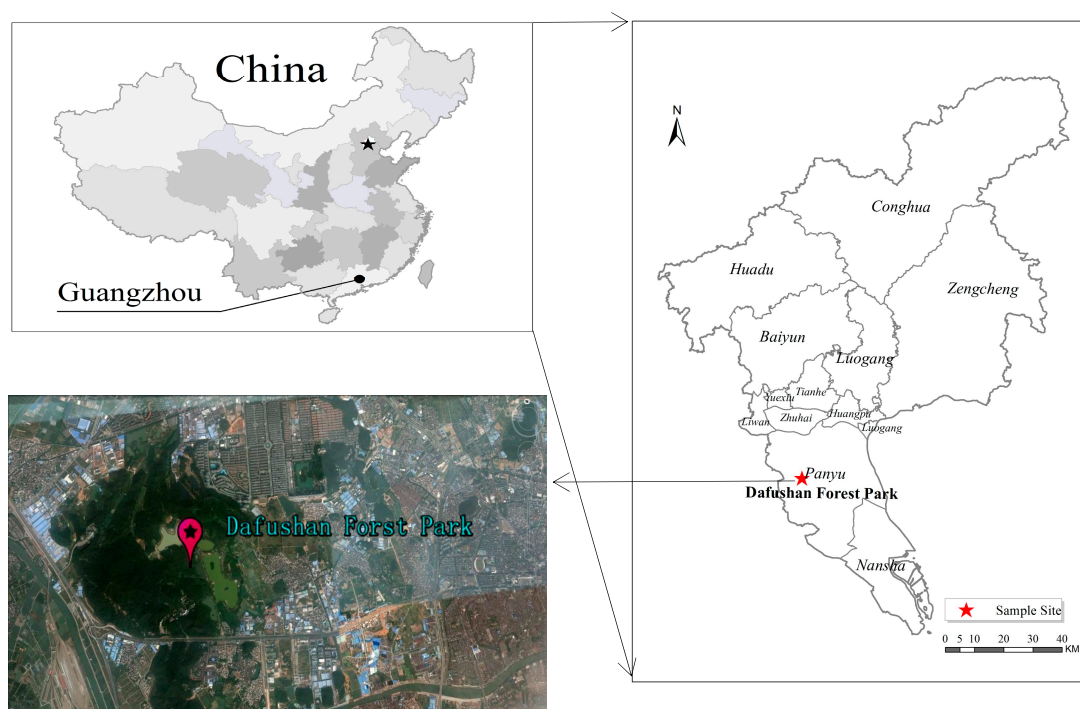


Table 4. Meteorological data for Dafushan forest park from 2008 to 2013 [26].

Season	Precipitation (mm)			Diurnal Relative Humidity (%)			Diurnal Air Temperature (°C)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
Rainy season	1383.4	1516.8	1296.2	88.3	98.8	40.6	25.1	35.3	11.6
Dry season	315.3	370.4	281.7	61.2	95.6	18.3	17.4	28.1	1.8

3.2. Sample Collection

Continuous 24-h TSP and PM_{2.5} samples were simultaneously collected using separate air samplers located at a height of 1.5 m above ground. To minimize the impact of vegetation or the forest canopy on the aerosols and the metal contents, and to obtain overall levels of air quality in this park, the instruments were placed at the open sites in the forest park and kept as far away as possible from the trees. The aerosol samples were trapped on the quartz-fiber (tare weighted before sampling) attached to the hopper of a moderate-volume sampler (TH 150-III, Wuhan, China) operating at a flow rate of 100 L·min^{−1}. Aerosols were collected 3 times per month according to the Forestry Standards “Observation Methodology for Long-term Forest Ecosystem Research” of China [46]. The total number of PM_{2.5} and TSP samples collected during the monitoring period from January 2012 to December 2013 was 72 (for each). Prior to sampling, the quartz-fiber, including the bank filters, were pre-heated in a muffle furnace at 600 °C for 3 h to remove the volatile components. After sampling, the filters were stored in a dessicator at a constant temperature (22 ± 0.5 °C) for 48 h and then re-weighed using a precision balance (Mettler Toledo Inc., Greifensee, Switzerland) to determine the mass of TSP and PM_{2.5}, respectively. Each filter was weighed at least three times, and the net mass was obtained by subtracting the pre-sampling weight from the post-sampling weight. The differences between replicate weights were less than 10 and 20 µg for the blanks and the samples, respectively. After weighting, the samples were stored in a freezer at −18 °C until to analysis to limit losses of volatile components.

3.3. Chemical Analyses

To quantify the concentrations of metals (Al, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, and Zn) in the TSP and PM_{2.5}, the filters were separately digested referring to the method of Lee *et al.* [34] and the national standards of PR China (GB/T 1526-94) for the determination of aerosol metal contents [47]. One half of each filter was soaked in a mixture of 10 mL of concentrated HNO₃ and H₂O₂ (v:v = 1:1) for 2 h and then heated to boiling for 10 min. After cooling down, the solution was added to 10 mL of H₂O₂ and heated until almost dry. Subsequently, 20 mL of diluted HNO₃ (with a concentration of 1%) was added and boiled for 10 min. The solution was then diluted with 1% HNO₃, poured into 50-mL volumetric flasks and finally filtered through polyethersulfone (PES) membrane filters (pore size: 0.45 µm, diameter: 13 mm; Membrana GmbH, Wuppertal, Germany). The blank filters were treated in a similar manner. The metal concentrations in the digestion solutions were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Angilent 7500cx, Tokyo, Japan). The limit of detection (LOD) for each metal was determined by measuring the signal to noise ratios. A signal to noise ratio of three was used to estimate the LOD. The LOD was 3.595 ng·m^{−3} for Al, Cu and Zn, 0.013 ng·m^{−3} for Cd, Co and Mo, 0.396 ng·m^{−3} for Cr and Pb, 0.03 ng·m^{−3} for Mn and Ni, 0.001 and 0.495 ng·m^{−3} for

Hg and Se, respectively. The experimental quality was controlled using blank filters and standard reference materials (US National Institute of Standards and Technology [NIST] standard reference materials (SRM 1648) Urban Particulate Matter, Gaithersburg, MD, USA). Five replicates of the standard SRM 1648 resulted in a minor recovery of 95.5% for Cu and a maximum recovery of 117% for Ni.

3.4. Statistical Analysis

A comparison of the PM and metal concentrations (mean and standard deviation, mean \pm SD) between the rainy and dry seasons was performed using one-way analysis of variance (ANOVA). Principal component analysis (PCA), a well-established method for aerosol analysis, was used to analyze the main sources of metals in the aerosols [39]. A PCA with Varimax rotation, which was performed using the software package SPSS (SPSS 17.0 for Windows, SPSS Inc., Chicago, IL, USA), was applied to the matrix of loads. Only the principal components with eigenvalues larger than 1.0 (before rotation) were retained for subsequent analysis and only the principal components with absolute loading values greater than 0.3 were considered [39].

4. Conclusions

The results of this case study revealed that Dafushan urban forest park at Guangzhou was polluted by PM_{2.5} rather than by TSP. The contents of both the PM_{2.5} and TSP were significantly higher in the dry season than in the rainy season. Aluminum, Zn, and Pb were the most abundant while Hg was the least abundant metals in the aerosols. Concentrations of Cd, Cu, Hg, Mn, Mo, Pb, and Zn in the TSP and PM_{2.5} were significantly higher in the dry season compared with the rainy season. The metals were predominant in the finer particles. The crustal enrichment factors implied that Cd, Cu, Mo, Pb, Se, and Zn in the aerosols in the forest park had anthropogenic sources, while Al and Mn were mainly of crustal origin. Results from the PCA implied that industrial activities, traffic-related emissions, and soil dust were the main possible sources of the metals in the PM_{2.5} and TSP in Dafushan forest park.

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Author Contributions

Fu-chun Tong, Shi-rong Liu, Yuan-wen Kuang, Bu-feng Chen and Yue-dong Guo were all involved in conceptualizing, designing, and implementing the project; Yi-hua Xiao performed the experiments. All data collected and drafted the manuscript by Yi-hua Xiao and Yuan-wen Kuang.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Espinosa, A.J.F.; Rodríguez, M.T.; Barragán de la Rosa, F.J.; Jiménez Sánchez, J.C. Size distribution of metals in urban aerosols in Seville (Spain). *Atmos. Environ.* **2001**, *35*, 2595–2601.
2. Pope, C.A.; Dockery, D.W. Health effects of fine particulate air pollution: Lines that connect. *J. Air Waste Manag. Assoc.* **2006**, *56*, 709–742.
3. Contini, D.; Cesari, D.; Donato, A.; Chirizzi, D.; Belosi, F. Characterization of PM₁₀ and PM_{2.5} and their metals content in different typologies of sites in South-Eastern Italy. *Atmosphere* **2014**, *5*, 435–453.
4. Duan, J.C.; Tan, J. Atmospheric heavy metals and arsenic in China: Situation, sources and control policies. *Atmos. Environ.* **2013**, *74*, 93–101.
5. Tao, J.; Ho, K.F.; Chen, L.G.; Zhu, L.H.; Han, J.L.; Xu, Z.C. Effect of chemical composition of PM_{2.5} on visibility in Guangzhou, China, 2007 spring. *Particuology* **2009**, *7*, 68–75.
6. Gralton, J.; Tovey, E.R.; McLaws, M.L.; Rawlinson, W.D. Respiratory virus RNA is detectable in airborne and droplet particles. *J. Med. Virol.* **2013**, *85*, 2151–2159.
7. He, K.M.; Wang, S.Q.; Zhang, J.L. Blood lead levels of children and its trend in China. *Sci. Total Environ.* **2009**, *407*, 3986–3993.
8. Bollati, V.; Marinelli, B.; Apostoli, P.; Bonzini, M.; Nordio, F.; Hoxha, M.; Pegoraro, V.; Motta, V.; Tarantini, L.; Cantone, L.; *et al.* Exposure to metal-rich particulate matter modifies the expression of candidate microRNAs in peripheral blood leukocytes. *Environ. Health Perspect.* **2010**, *118*, 763–768.
9. Zabala, J.; Ogulei, D.; Hopke, P.K.; Lee, J.H.; Hwang, I.; Querol, X.; Alastuey, A.S.; Santamaría, J.S. Concentration and sources of PM₁₀ and its constituents in Alsasua, Spain. *Water Air Soil Pollut.* **2006**, *174*, 385–404.
10. Zheng, N.; Liu, J.S.; Wang, Q.C.; Liang, Z.Z. Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, northeast of China. *Sci. Total Environ.* **2010**, *408*, 726–733.
11. Tian, H.Z.; Wang, Y.; Xue, Z.G.; Cheng, K.; Qu, Y.P.; Chai, F.H. Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980–2007. *Atmos. Chem. Phys.* **2010**, *10*, 11905–11919.
12. El-Fadel, M.; Hashisho, Z. Vehicular emissions in roadway tunnels: A critical review. *Crit. Rev. Environ. Sci. Technol.* **2001**, *31*, 125–174.
13. Kothai, P.; Saradhi, I.V.; Prathibha, P.; Hopke, P.K.; Pandit, G.G.; Puranik, V.D. Source apportionment of coarse and fine particulate matter at Navi Mumbai, India. *Aerosol. Air Qual. Res.* **2008**, *8*, 423–436.
14. Chang, S.H.; Wang, K.S.; Chang, H.F.; Ni, W.W.; Wu, B.J.; Wong, R.H.; Lee, H.S. Comparison of source identification of metals in road-dust and soil. *Soil Sediment Contam.* **2009**, *18*, 669–683.
15. Fang, G.C.; Chang, C.N.; Wu, Y.S.; Wang, V.; Fu, P.P.C.; Yang, D.G.; Chen, S.C.; Chu, C.C. The study of fine and coarse particles, and metallic elements for the daytime and night-time in a suburban area of central Taiwan, Taichung. *Chemosphere* **2000**, *41*, 639–644.
16. Fang, G.C.; Wu, Y.S.; Chang, S.Y.; Huang, S.H.; Rau, J.Y. Size Distributions of ambient air particles and enrichment factor analyses of metallic elements at Taichung Harbor near the Taiwan Strait. *Atmos. Res.* **2006**, *81*, 320–333.

17. Duan, J.C.; Tan, J.H.; Cheng, D.X.; Bi, X.H.; Deng, W.J.; Sheng, G.Y.; Fu, J.M.; Wong, M.H. Sources and characteristics of carbonaceous aerosol in two largest cities in Pearl River Delta Region, China. *Atmos. Environ.* **2007**, *41*, 2895–2903.
18. Wang, X.H.; Bi, X.H.; Sheng, G.Y.; Fu, J.M. Hospital indoor PM₁₀/PM_{2.5} and associated trace elements in Guangzhou, China. *Sci. Total. Environ.* **2006**, *366*, 124–135.
19. Cao, J.J.; Shen, Z.X.; Chow, J.C.; Watson, J.G.; Lee, S.C.; Tie, X.X.; Ho, K.F.; Wang, G.H.; Han, Y.M. Winter and summer PM_{2.5} chemical compositions in fourteen Chinese cities. *J. Air Waste Manag.* **2012**, *62*, 1214–1226.
20. Niu, L.L.; Ye, H.J.; Xu, C.; Yao, Y.J.; Liu, W.P. Highly time- and size-resolved fingerprint analysis and risk assessment of airborne elements in a megacity in the Yangtze River Delta, China. *Chemosphere* **2015**, *119*, 112–121.
21. Zhao, P.S.; Dong, F.; He, D.; Zhao, X.J.; Zhang, X.L.; Zhang, W.Z.; Yao, Q.; Liu, H.Y. Characteristics of concentrations and chemical compositions for PM_{2.5} in the region of Beijing, Tianjin, and Hebei, China. *Atmos. Chem. Phys.* **2013**, *13*, 4631–4644.
22. Li, L.; Wang, W.; Feng, J.; Zhang, D.; Li, H.; Gu, Z.P.; Wang, B.J.; Sheng, G.Y.; Fu, J.M. Composition, source, mass closure of PM_{2.5} aerosols for four forests in eastern China. *J. Environ. Sci.* **2010**, *22*, 405–412.
23. Li, S.N.; Lu, S.W.; Pan, Q.H.; Zhang, Y.P.; Chen, B.; Yang, X.Y. Research on the eco-purification function of urban forests in Beijing. *J. Food Agric. Environ.* **2013**, *11*, 1247–1254.
24. Sun, F.B.; Yin, Z.; Lun, X.X.; Zhao, Y.; Li, R.N.; Shi, F.T.; Yu, X.X. Deposition velocity of PM_{2.5} in the winter and spring above deciduous and coniferous forests in Beijing, China. *PLoS One* **2014**, doi:10.1371/journal.pone.0097723.
25. Statistical Bureau of Guangdong Province. *Guangdong Year Book (1950–2012)*; Guangdong Publishing House: Guangzhou, China, 2013. (In Chinese)
26. Xiao, Y.H.; Chen, B.F.; Su, J.; Yu, R.; Pan, Y.J.; Shi, X.; Chen, J. Variations of air pollutant concentrations and their evaluation in Dafushan forest park, a case in Guangzhou. *J. Chin. Urban For.* **2010**, *8*, 43–45. (In Chinese)
27. Ministry of Environmental Protection. Ambient Air Quality Standards (GB 3095-1996). 2012. Available online: <http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqhjlz/201203/W020120302359392037286.pdf> (accessed on 29 August 2014). (In Chinese)
28. Huang, H.; Lee, S.C.; Cao, J.J.; Zou, C.W.; Chen, X.G.; Fan, S.J. Characteristics of indoor/outdoor PM_{2.5} and elemental components in generic urban, roadside and industrial plant areas of Guangzhou city, China. *J. Environ. Sci.* **2007**, *19*, 35–43.
29. Maenhaut, W.; Raes, N.; Chi, X.G.; Cafmeyer, J.; Wang, W. Chemical composition and mass closure for PM_{2.5} and PM₁₀ aerosols at K-puszta, Hungary, in summer 2006. *X-ray Spectrom.* **2008**, *37*, 193–197.
30. Hock, N.; Schneider, J.; Borrmann, S.; Rompp, A.; Moortgat, G.; Franze, T.; Schauer, C.; Pöschl, U.; Plass-Dülmer, C.; Berresheim, H. Rural continental aerosol properties and processes observed during the Hohenpeissenberg Aerosol Characterization Experiment (HAZE2002). *Atmos. Chem. Phys.* **2008**, *8*, 603–623.

31. Edney, E.O.; Kleindienst, T.E.; Conver, T.S.; McIver, C.D.; Corse, E.W.; Weathers, W.S. Polar organic oxygenates in PM_{2.5} at a southeastern site in the United States. *Atmos. Environ.* **2003**, *37*, 3947–3965.
32. Pillai, P.S.; Babu, S.S.; Krishna, M.K. A Study of PM, PM₁₀ and PM_{2.5} concentration at a tropical coastal station. *Atmos. Res.* **2002**, *61*, 149–167.
33. Glavas, S.D.; Nikolakis, P.; Ambatzoglou, D.; Mihalopoulos, N. Factors affecting the seasonal variation of mass and ionic composition of PM_{2.5} at a central Mediterranean coastal site. *Atmos. Environ.* **2008**, *42*, 5365–5373.
34. Lee, C.S.L.; Li, X.D.; Zhang, G.; Li, J.; Ding, A.J.; Wang, T. Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, south China—Evidence of the long-range transport of air contaminants. *Atmos. Environ.* **2007**, *41*, 432–447.
35. Cesari, D.; Contini, D.; Genga, A.; Siciliano, M.; Elefante, C.; Baglivi, F.; Daniele L. Analysis of raw soils and their re-suspended PM₁₀ fractions: Characterisation of source profiles and enrichment factors. *Appl. Geochem.* **2012**, *27*, 1238–1246.
36. Soil Census Office of Guangdong province. *Guangdong Soil*; Science Press: Beijing, China, 1993. (In Chinese)
37. Dongarrà, G.; Manno, E.; Varrica, D.; Voltaggio, M. Mass levels, crustal component and trace elements in PM₁₀ in Palermo, Italy. *Atmos. Environ.* **2007**, *41*, 7977–7986.
38. Henry, R.C.; Lewis, C.W.; Hopke, P.K.; Williamson, H.J. Review of receptor model fundamentals. *Atmos. Environ.* **1984**, *18*, 1507–1515.
39. Contini, D.; Belosi, F.; Gambaro, A.; Cesari, D.; Stortini, A.M.; Bove, M.C. Comparison of PM₁₀ concentrations and metal content in three different sites of the Venice Lagoon: An analysis of possible aerosols sources. *J. Environ. Sci.* **2012**, *24*, 1954–1965.
40. Contini, D.; Genga, A.; Cesari, D.; Siciliano, M.; Donato, A.; Bove, M.C.; Guascito, M.R. Characterisation and source apportionment of PM₁₀ in an urban background site in Lecce. *Atmos. Res.* **2010**, *95*, 40–54.
41. Baumann, K.; Jayanty, R.K.M.; Flanagan, J.B. Fine particulate matter source apportionment for the chemical speciation trends network site at Birmingham, Alabama, using positive matrix factorization. *J. Air Waste Manag. Assoc.* **2008**, *58*, 27–44.
42. Fung, Y.S.; Wong, L.W.Y. Apportionment of air pollution sources by receptor models in Hong Kong. *Atmos. Environ.* **1995**, *29*, 2041–2048.
43. Stortini, A.M.; Freda, A.; Cesari, D.; Cairns, W.R.L.; Contini, D.; Barbante, C.; Prodi, F.; Cescon, P.; Gambaro, A. An evaluation of the PM_{2.5} trace elemental composition in the Venice Lagoon area and an analysis of the possible sources. *Atmos. Environ.* **2009**, *43*, 6296–6304.
44. Janssen, N.; van Mansom, D.F.M.; van der Jagt, K.; Harseema, H.; Hoek, G. Mass concentration and elemental composition of airborne particulate matter at street and background locations. *Atmos. Environ.* **1997**, *31*, 1185–1193.
45. Manoli, E.; Voutsas, D.; Samara, C. Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece. *Atmos. Environ.* **2002**, *36*, 949–961.

46. “Observation Methodology for Long-term Forest Ecosystem Research” of People’s Republic of China. Available online: http://www.cfern.org/wjpicture/upload/bzgf/bzgf_2011-10-10-8-13-39.pdf (accessed on 29 August 2014). (In Chinese)
47. Ministry of Environmental Protection. Ambient Air-Determination of Lead-Flame Atomic Absorption Spectrophotometric Method (GB/T 15264-94). 1995. Available online: <http://www.shuigongye.com/standard/20096/2009061816220200001.html> (accessed on 2 September 2014).

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