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Local and regional anthropogenic influence on $PM_{2.5}$ elements in Hong Kong

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Abstract

Hong Kong's persistent unhealthy level of fine particulate matter is a current public health challenge, complicated by the city being located in the rapidly industrializing Pearl River Delta Region of China. While the sources of the region's fine particulate matter ($PM_{2.5}$) are still not well understood, this study provides new source information through ground measurements and statistical analysis of 24 elements associated with particulate matter collected on filters. Field measurements took place over 4 months (October 2002, December 2002, March 2003, and June 2003) at seven sites throughout the Pearl River Delta, with three sites located in Hong Kong and four sites in the neighboring province, Guangdong. The 4-month average element concentrations show significant variation throughout the region, with higher levels of nearly every species seen among the northern Guangdong sites in comparison to Hong Kong. The high correlation (Pearson $r > 0.8$) and similar magnitudes of 11 species (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb) at three contrasting sites in Hong Kong indicate that sources external to Hong Kong dominate the regional levels of these elements. Further correlative analysis compared Hong Kong against potential source areas in Guangdong Province (Shenzhen, Zhongshan, and Guangzhou). Moderate correlation of sulfur for all pairings of Hong Kong sites with three Guangdong sites in developed areas (average Pearson r of 0.52–0.94) supports the importance of long-distance transport impacting the region as a whole, although local sources also clearly impact observed concentrations. Varying correlative characteristics for zinc when Hong Kong sites are paired with Shenzhen (average $r = 0.86$), Guangzhou (average $r = -0.65$) and Zhongshan (average $r = 0.45$) points to a source area located south of Guangzhou and locally impacting Zhongshan. The concentration distribution and correlative characteristics of bromide point to sources located within the Pearl River Delta, but the specific location is yet inconclusive. Uniquely poor correlation of eight species (Al, Si, K, Ca, Mn, Fe, Rb, and Pb)

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for the pairing of Hong Kong sites with Guangzhou, in addition to the relatively higher concentrations measured at Guangzhou, indicates a significant regional impact due to land development and industrial activities in the Guangzhou vicinity.

Keywords: Pearl River Delta; Elements; $PM_{2.5}$; Source areas; Correlation

1. Introduction

Located within the rapidly developing Pearl River Delta Region of China, the city of Hong Kong suffers poor air quality that frequently obscures the city's skyline and poses a health threat to its residents. Among the air pollutants that comprise urban smog, particulate pollution in China has been shown to be of significant concern for its negative effects on the respiratory and cardiological function of adults and children (Wong et al., 2002, 2006; Zhang et al., 2002). Secondary impacts of particulate pollution include the alteration of local climate (Haywood and Shine, 1995; Schwartz, 1996) and a reduction in visibility. Fine particles, air-suspended solid and liquid particles with a diameter less than 2.5 μm ($PM_{2.5}$), are intrinsically challenging to control with numerous natural and anthropogenic sources and a residence time in the lower atmosphere (days to weeks) allowing for transport up to thousands of kilometers.

The management of fine particulate pollution in Hong Kong is difficult due to the area's physical and economic geography. Hong Kong is part of the Pearl River Delta Region, a highly populated (46 million) and developed area surrounding the mouth of the Pearl River (Zhujiang). The population of Hong Kong (6.8 million) is located within the valley regions of 1100 km^2 land area that consists of several mountainous islands and a peninsula attached to China's mainland. Also incorporated in the Pearl River Delta Region is the southern section of Guangdong Province, including the major cities of Guangzhou (population of 7.5 million), Zhongshan (1.4 million) and Shenzhen (1.8 million) (Guangdong Statistical Yearbook, 2006). Guangdong Province, located north of Hong Kong, has captured recent attention for its rampant industrial growth and associated emissions of atmospheric pollutants (Streets et al., 2006). Although Hong Kong is primarily associated with service industries, it also has local sources of air pollutants such as vehicular traffic, shipping, cooking, and manufacturing.

Recent measurements of fine particulate matter in Hong Kong and neighboring Guangdong (Cao et al., 2003, 2004; Cohen et al., 2004; Hagler et al., 2006; Louie et al., 2005a; Pathak et al., 2003; Qian et al., 2001; Wei et al., 1999) have confirmed the existence of unhealthy concentrations well-exceeding the current World Health Organization Air Quality Guidelines (AQG) of 10 $\mu g\,m^{-3}$ (annual average) and 25 $\mu g\,m^{-3}$ (24 h average) (WHO (World Health Organization), 2006). Given the complex nature of air quality in the quickly developing Pearl River Delta, ground measurements are valuable in linking emissions inventories with ambient concentrations and in supporting the accuracy of regional air quality modeling. In addition, source information derived from ground measurements can be useful in the development of effective strategies to alleviate Hong Kong's particulate pollution. Previous studies, limited to measurement in the Hong Kong area, provided fine particulate source information through the analysis of chemical composition (Cohen et al., 2004; Louie et al., 2005a; Zheng et al., 2000) and in combining chemical speciation with local meteorology (Louie et al., 2005b; Pathak et al., 2003).

Our previous paper (Hagler et al., 2006) presented the first attempt to determine source areas simultaneously in both Hong Kong and Guangdong Province by comparing meteorological trends and specific particulate matter species (overall fine particle mass, organic carbon, elemental carbon, sulfate, lead, and potassium). This current study complements our previous analysis by deriving information on sources and source locations of fine particulate matter affecting Hong Kong through the spatial and correlative characteristics of 24 elements measured at seven sites in the Pearl River Delta Region.

2. Methodology

The field sampling and ensuing chemical analysis have been previously discussed in detail (Hagler et al., 2006). Briefly, 4 months of field sampling

(October and December, 2002; March and June, 2003) took place at seven sites in the Pearl River Delta with three sites located in Hong Kong and four in Guangdong Province. The location of sampling sites and their characteristics are displayed in Fig. 1. Samples of fine particulate matter were collected for 24 h each 6th day, with 20 total measurement periods at each site. Ambient particulate matter was collected in four parallel channels (two quartz fiber filters, two Teflon filters) with a cyclone-based size selection of particles less than 2.5 μm in diameter ($PM_{2.5}$). After sample collection, filters were kept sealed in Petri dishes and at a low temperature ($T<0\,°C$) until later laboratory analysis for total mass, major ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+), elemental carbon (EC), organic carbon (OC), and elements. Ion chromatography was used to determine major anions, while ammonium was measured with indophenol colorimetric analysis. Carbonaceous species (EC and OC) were quantified using a Sunset Laboratory carbon analyzer, following the NIOSH method of thermal evolution and combustion (Birch and Cary, 1996).

Specific elements were detected using X-ray fluorescence analysis (XRF), including sulfur (S), potassium (K), silica (Si), zinc (Zn), iron (Fe), sodium (Na), calcium (Ca), lead (Pb), aluminum (Al), manganese (Mn), copper (Cu), vanadium (V), arsenic (As), tin (Sn), bromide (Br), rubidium (Rb), nickel (Ni), selenium (Se), thallium (Tl), chromium (Cr), cobalt (Co), and strontium (Sr) (Watson et al., 1996). Crustal (EF) and seawater (SEF) enrichment factors were calculated to compare the composition of the ambient particulate matter samples with the average elemental composition of Earth's crust and ocean water (Weast, 1987). The EF is calculated as follows: $EF = (X_i/Al)_{sample}/(X_i/Al)_{crust}$, where X_i is a given element concentration and aluminum (Al) is assumed to be entirely from Earth's crust. Similarly, seawater enrichment factor (SEF) is calculated as $SEF = (X_i/Na)_{sample}/(X_i/Na)_{ocean}$, where sodium (Na) is likewise assumed to solely originate from seaspray.

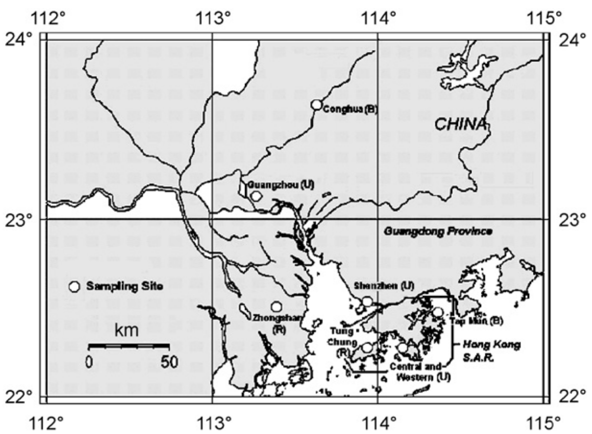

Fig. 1. Location of sampling sites in the Hong Kong Special Administrative Region (SAR) and Guangdong Province. Letters U, R, and B denote urban locations, receptor locations in close proximity to urban areas, and rural background sites, respectively.

3. Results and discussion

3.1. Trace element enrichment and concentrations

With the main aim of this analysis to determine sources and locations of sources affecting $PM_{2.5}$ in Hong Kong, crustal (EF) and seawater (SEF) enrichment factors provide the ability to determine which elements may be mainly of crustal or oceanic origin. Given that the Pearl River Delta is located near the ocean and has no local volcanic activity, elements highly enriched relative to both crustal and oceanic sources are most likely originated from anthropogenic activity. However, it is also possible that human activity in land development may contribute to elements of apparent crustal origin (low EF). Shown in Fig. 2, low enrichment factors ($EF<5.0$) are found for Si, Ca, Sr, and Fe indicating that fine particulate levels of these species are most likely dominated by crustal material. In contrast, all other species are seen to be impacted by non-crustal sources, with very high enrichment ($EF>1000$) observed for elements Zn, Tl, Br, Sn, As, S, Pb, and Se. In addition to the general grouping of elements by enrichment factor, the relative range of enrichment factors among the monitoring sites gives clues to the possible presence of sources. Among the highly enriched species, Cr, Ni, and As are seen to have high outliers occur at certain monitoring sites. Chromium and Ni both have significantly high enrichment factors at Zhongshan, with Shenzhen also highly enriched in Ni. Guangzhou stands out for highest enrichment in many species, with a particularly high As-enrichment in comparison with other sites in the area.

The influence of the surrounding ocean was similarly estimated by comparing the ratio of measured elements to measured Na with their associated seawater ratio. The only species with a low SEF at all sites is Cl (4-month average

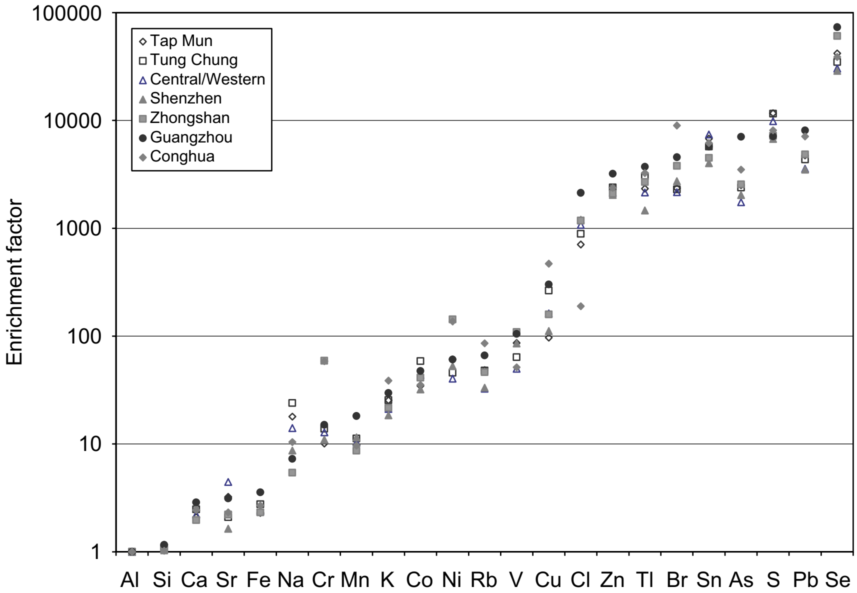

Fig. 2. Four-month average enrichment factors of elements at seven sites in the Pearl River Delta Region of China.

SEF = 0.1–0.9), with below-unity values expected as a chloride depletion reaction with nitrate is known to occur (Ho et al., 2003; Lee et al., 1999), the loss mechanism also making it difficult to determine from only its enrichment level whether the species is solely originated from the ocean. It is also of note that bromide is seen to have low enrichment at sites in Hong Kong (SEF = 1.6–2.6), though higher enrichment is observed at sites in Guangdong (SEF = 5.4–14.7), indicating a combination of oceanic and anthropogenic sources of bromide in the region. It is interesting that the Guangdong rural site, Conghua, has significantly higher bromide enrichment than elsewhere in the region. Potassium (K) and sulfur (S) are two species that are often used to indicate biomass burning and coal combustion, respectively, though they may each also have an oceanic component (Watson et al., 2001). In the Pearl River Delta, the high SEF values of K (26–100) and S (63–174) demonstrate that the ocean plays a minor role in the measured particulate levels of these species.

While enrichment factors may indicate natural (oceanic and crustal sources) versus anthropogenic sources, spatial differences in element concentrations can point to potential source locations. The average element concentrations over the entire measurement period (October 2002, December 2002, March 2003, and June 2003) are summarized in Table 1. The average levels recorded in this study are similar to values measured by past researchers at comparable sites (urban and rural) within Hong Kong (Cohen et al., 2004; Ho et al., 2003; Louie et al., 2005a) and in the city of Guangzhou (Wei et al., 1999). It is immediately striking to note that, with the exception of sodium, each measured element is highest at a Guangdong site and most frequently at urban Guangzhou. In fact, Guangzhou stands out as a significant industrial source area with average levels more than 30% higher than any other site for highly enriched (EF > 1000) Zn, Tl, As, Pb, and Se. It is also interesting to note that species exhibiting crustal characteristics (EF < 5) are also seen to have significantly higher levels in Guangdong Province compared with Hong Kong, indicating that human activity in Guangdong Province may be increasing crustal material concentrations in the Pearl River Delta.

Among the Hong Kong sites, a difference in concentration between remote Tap Mun and more developed Central/Western and Tung Chung may point to the influence of local human activity on Hong Kong's air quality. For the majority of the species, the three sites are observed to be within close range of one another. However, a difference in concentration exceeding 50% is observed among the three sites for eight species (EC, Cl, V, Cr, Co, Cu, Sr, and Sn), pointing to local emissions. Vehicular emissions may be linked to a local spatial difference in EC (diesel exhaust) and Cu (brake

Table 1
Elemental composition of $PM_{2.5}$ ($\mu g\,m^{-3}$)

Species	Tap Mun			Tung Chung			Central/Western			Shenzhen			Zhongshan			Guangzhou			Conghua		
	N	Avg	CV[a]	*N*	Avg	CV	*N*	Avg	CV	*N*	Avg	CV	*N*	Avg	CV	*N*	Avg	CV	*N*	Avg	CV
$PM_{2.5}$	20	2.9E+01	0.48	20	3.2E+01	0.45	20	3.4E+01	0.41	21	4.7E+01	0.45	19	4.6E+01	0.49	20	7.1E+01	0.43	19	3.7E+01	0.50
S	20	3.2E+00	0.55	20	3.1E+00	0.60	20	3.2E+00	0.51	21	3.5E+00	0.52	19	4.3E+00	0.47	20	4.9E+00	0.42	19	3.9E+00	0.50
EC	20	8.2E−01	0.58	20	2.0E+00	0.48	20	1.9E+00	0.52	21	3.9E+00	0.58	19	2.5E+00	0.50	20	4.4E+00	0.40	19	1.4E+00	0.36
K	20	5.7E−01	0.75	20	5.6E−01	0.73	20	5.6E−01	0.75	21	8.6E−01	0.63	19	1.0E+00	0.98	20	1.7E+00	0.53	19	1.5E+00	0.55
Na	17	4.5E−01	0.71	15	5.9E−01	0.54	19	4.2E−01	0.49	20	5.5E−01	0.89	17	2.9E−01	0.51	20	4.3E−01	0.67	17	4.5E−01	0.63
Si	20	3.5E−01	0.81	20	3.1E−01	0.79	20	3.5E−01	0.75	21	6.1E−01	0.57	19	6.8E−01	0.72	20	8.8E−01	0.48	19	5.3E−01	0.56
Zn	20	1.8E−01	0.81	20	1.7E−01	0.83	20	1.9E−01	0.64	21	3.1E−01	0.66	19	3.3E−01	0.84	20	6.1E−01	0.53	19	3.1E−01	0.68
Fe	20	1.4E−01	0.75	20	1.6E−01	0.68	20	1.7E−01	0.59	21	2.9E−01	0.48	19	3.0E−01	0.65	20	5.3E−01	0.75	19	2.8E−01	0.60
Cl	20	9.3E−02	0.84	20	1.1E−01	0.77	20	1.2E−01	0.67	21	2.3E−01	0.74	19	1.9E−01	0.94	20	3.2E−01	0.51	19	1.9E−01	0.54
Ca	20	8.9E−02	0.73	20	8.7E−02	0.88	20	1.1E−01	0.74	21	1.7E−01	0.61	19	1.9E−01	0.71	20	2.3E−01	0.63	19	1.5E−01	0.58
Al	19	6.3E−02	0.77	20	5.7E−02	0.82	19	5.6E−02	0.71	21	1.0E−01	0.77	19	1.4E−01	0.87	20	2.7E−01	0.43	19	1.6E−01	0.60
Pb	17	1.5E−02	1.08	16	1.2E−02	0.62	17	1.9E−02	0.59	19	1.6E−02	0.63	16	2.0E−02	0.58	19	3.0E−02	0.61	19	2.3E−02	0.82
Sn	20	1.1E−02	0.86	20	7.2E−03	0.81	20	6.8E−03	1.20	21	2.1E−02	0.67	19	3.4E−02	0.63	20	3.6E−02	0.66	19	9.8E−03	1.12
V	14	1.0E−02	0.98	13	1.2E−02	0.74	11	9.8E−03	0.78	19	2.3E−02	0.62	16	2.7E−02	0.82	19	3.2E−02	0.60	17	1.6E−02	1.11
Mn	20	1.0E−02	0.69	20	1.1E−02	0.65	20	1.2E−02	0.56	21	2.5E−02	0.51	19	1.9E−02	0.64	20	4.4E−02	1.15	19	1.7E−02	0.68
Br	20	6.3E−03	0.73	20	6.0E−03	0.61	20	6.8E−03	0.64	21	1.8E−02	1.02	19	2.2E−02	0.89	20	2.8E−02	0.97	18	4.3E−02	1.36
Cu	19	5.7E−03	0.71	20	1.5E−02	0.30	20	1.1E−02	0.49	21	1.4E−02	0.62	19	2.0E−02	0.74	20	4.3E−02	0.55	19	4.9E−02	1.06
Ni	20	4.9E−03	0.59	20	3.6E−03	0.77	20	3.8E−03	0.61	21	8.2E−03	0.55	19	2.4E−02	0.98	20	1.2E−02	0.63	19	2.0E−02	0.48
As	17	4.8E−03	0.66	17	4.5E−03	0.71	17	4.0E−03	0.82	19	8.7E−03	0.67	18	1.0E−02	0.80	20	3.4E−02	0.43	19	1.2E−02	0.75
Rb	19	4.7E−03	0.74	18	4.5E−03	0.71	20	3.7E−03	0.79	21	6.9E−03	0.73	19	9.5E−03	1.10	20	1.6E−02	0.58	19	1.4E−02	0.60
Se	18	2.2E−03	0.60	19	1.8E−03	0.71	20	1.9E−03	0.69	20	3.3E−03	0.67	18	6.9E−03	0.84	20	1.1E−02	0.92	19	3.6E−03	0.60
Sr	14	1.3E−03	0.58	16	8.2E−04	0.75	16	2.1E−03	1.43	20	1.2E−03	0.67	18	1.9E−03	0.70	16	3.1E−03	0.53	18	1.6E−03	0.93
Tl	18	1.1E−03	1.05	17	1.4E−03	0.47	15	1.2E−03	0.80	16	1.6E−03	0.81	18	2.8E−03	0.83	19	4.6E−03	0.48	18	2.8E−03	0.71
Cr	16	1.1E−03	0.62	14	1.4E−03	0.50	16	1.6E−03	0.63	19	2.6E−03	0.89	19	1.3E−02	1.43	18	3.9E−03	0.63	19	1.2E−02	0.61
Co	20	9.3E−04	0.53	20	1.5E−03	0.61	20	1.4E−03	0.56	20	1.9E−03	0.77	19	2.3E−03	0.75	20	3.1E−03	0.71	19	1.7E−03	0.70

[a]Coefficient of variation.

wear) (Lough et al., 2005). A second possible source of Cu in the Hong Kong area is local printed circuit board manufacturing (Qin et al., 1997), although this industry may have since been relocated to other areas in the Pearl River Delta. While spatial variability in Hong Kong is commonly seen with elevated concentrations in urban areas, it is of note that both Ni and V are, on average, at increased levels (32% and 43% higher, respectively) at the remote Tap Mun island compared with the more developed sites in Hong Kong. The presence of Ni and V in the Hong Kong area has been previously related to fuel oil combustion (Lee et al., 1999) and thus the concentrations observed at Tap Mun may be linked to local shipping activity.

3.2. Spatial correlation analysis

Inter-site correlation provides additional evidence on the relative influence of local versus regional sources. Figs. 3a–d show examples of the information obtained by comparing two sites in Hong Kong situated in developed areas (Central/Western and Tung Chung) with a site located in an undeveloped region (Tap Mun). It is seen that S and K levels appear to have similar characteristics at both the rural and urban sites, having high correlation ($R^2 > 0.76$) and comparable concentrations. This strong relationship suggests that the Hong Kong area is affected regionally by exterior sources for both species. Sulfur, usually found as a sulfate ion in particulate matter, is typically associated with the

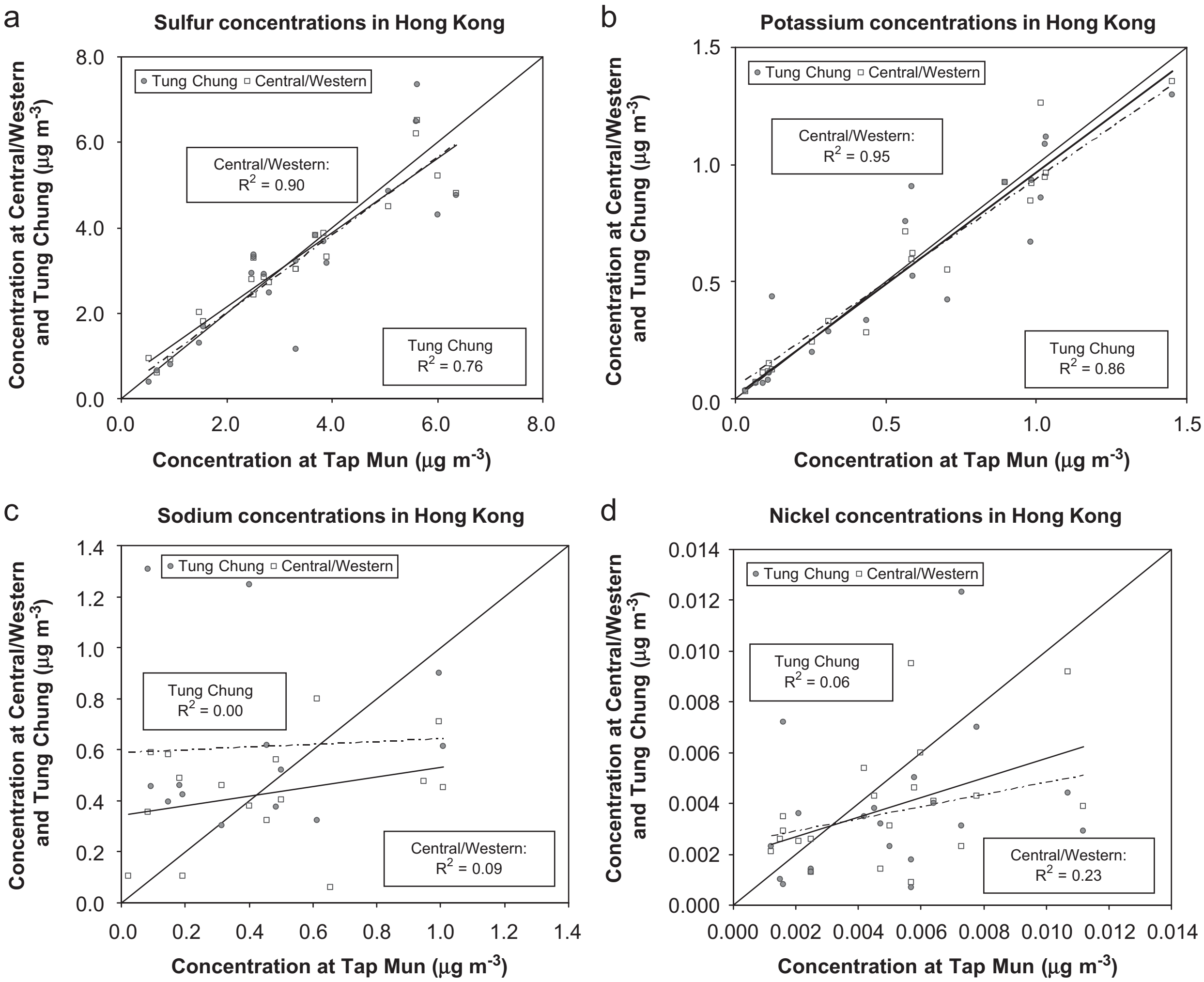

Fig. 3. Several elements measured at the Hong Kong background site, Tap Mun, compared with at the more developed sites in Hong Kong, Central/Western and Tung Chung.

combustion of coal burning while K is often linked with biomass burning (Watson et al., 2001), although incineration has also been suggested as another important source of K in the Pearl River Delta (Louie et al., 2005a). In comparison, Na and Ni show very little relationship among the sites in Hong Kong ($R^2 < 0.23$), indicating that local sources (oceanic and fuel oil, respectively) may be important in controlling their levels. This analysis of correlative characteristics was extended to all 24 elements, with the inter-site Pearson correlation coefficients displayed in Fig. 4. Based upon this analysis, 11 of the 24 elements (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb) exhibit strong inter-site correlation for the Hong Kong sites (average Pearson $r > 0.8$) and thus appear to be controlled by sources outside of Hong Kong. In contrast, the remaining species (Na, Cl, V, Cr, Co, Ni, Cu, As, Se, Sr, Sn, Tl, and EC) appear to be influenced to varying degrees by local natural and anthropogenic sources.

While high correlation between sites in Hong Kong may be due to transport of external emissions into the Hong Kong area, the strong relationship between sites could also be induced by a locally distributed source that undergoes similar patterns among sites due to meteorology. However, additional evidence of similar element magnitudes would add support to the conclusion that an external source impacts the Hong Kong area equally. To further test that the 11 highly correlated elements (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb) are controlled by sources exterior to Hong Kong, a linear least-squares fit was calculated for these species, using the rural Hong Kong site, Tap Mun, as an independent predictor of concentrations at the two Hong Kong sites in developed locations (Central/Western and Tung Chung). It can be seen in Table 2 that the linear fit for each species has a calculated slope in the range of 0.8–1.1, with the significance of the slope represented by t-values well-exceeding 2.0. In addition, the calculated intercept is shown to be minor to negligible for each species. This demonstrates how concentrations of the selected species increase and decrease in a nearly equal fashion among the entire Hong Kong region, indicating that exterior sources influence the Hong Kong area as a whole.

The next step of analysis was to determine whether sources of the 11 species are located within the Pearl River Delta or at a further distance from Hong Kong. Correlating the levels of Hong Kong sites against potential nearby source areas (sites in developed areas of Guangdong Province—Shenzhen, Zhongshan, and Guangzhou) provides useful information about source location. High correlation with nearby developed areas in Guangdong Province would indicate that long-distance transport is the dominant mechanism controlling a species throughout the entire region, while low correlation indicates a local source area is important.

Figs. 5a–c show the correlation of the selected species (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb)

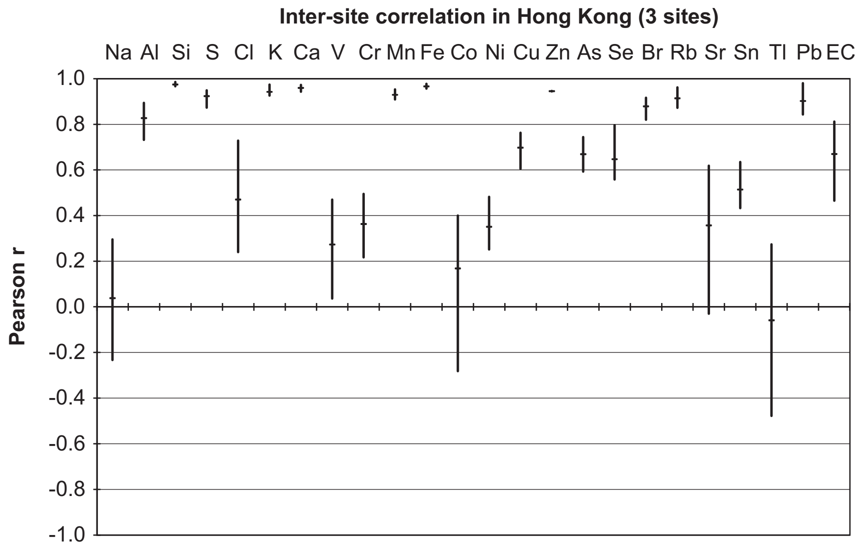

Fig. 4. Pearson correlation coefficient calculated between pairings of Hong Kong sites Tap Mun, Tung Chung, and Central/Western. Markers denote the average of the three correlations, with bars stretching from maximum to minimum correlation coefficient.

for pairings of the Hong Kong sites with Shenzhen, Zhongshan, and Guangzhou, respectively. In Fig. 5a, it appears that Shenzhen has a close relationship with Hong Kong for nearly all species, with high correlation (average Pearson $r > 8.0$) for eight species (Si, S, K, Ca, Fe, Zn, Rb, and Pb) and moderate correlation (average Pearson $r > 6.0$) for two others (Al and Mn). However, Br appears to have a weaker

Table 2
Least-squares fit of developed sites in Hong Kong versus rural Tap Mun

Species	Tung Chung versus Tap Mun				Central and Western versus Tap Mun			
	Slope[a]	t[b]	Intercept	t	Slope	t	Intercept	t
Al	0.86±0.39	4.6	0.010±0.043	0.5	1.07±0.27	8.5	0.010±0.030	0.7
Si	0.84±0.11	16.0	0.018±0.049	0.8	0.91±0.08	24.7	0.028±0.035	1.7
K	0.89±0.18	10.4	0.052±0.127	0.9	0.96±0.11	18.3	0.013±0.078	0.4
Ca	1.00±0.18	12.0	0.014±0.021	1.4	0.97±0.12	17.7	0.025±0.014	3.9
Mn	0.96±0.19	10.4	0.001±0.003	1.3	0.95±0.15	13.3	0.003±0.002	3.3
Fe	1.02±0.14	15.3	0.021±0.024	1.9	0.93±0.14	13.8	0.041±0.024	3.6
Zn	0.94±0.16	12.2	0.006±0.037	0.3	0.79±0.13	12.5	0.047±0.031	3.2
Rb	0.80±0.25	6.9	0.001±0.002	0.9	0.81±0.12	14.5	0.000±0.001	0.2
Pb	0.80±0.26	6.5	0.009±0.021	0.9	0.80±0.08	20.3	0.005±0.007	1.7

[a]Value is the calculated best-fit slope or intercept ± the parameters 95% confidence interval, using the Tap Mun concentrations of each element as the independent variable.
[b]The t-value is the estimated regression coefficient divided by its standard error.

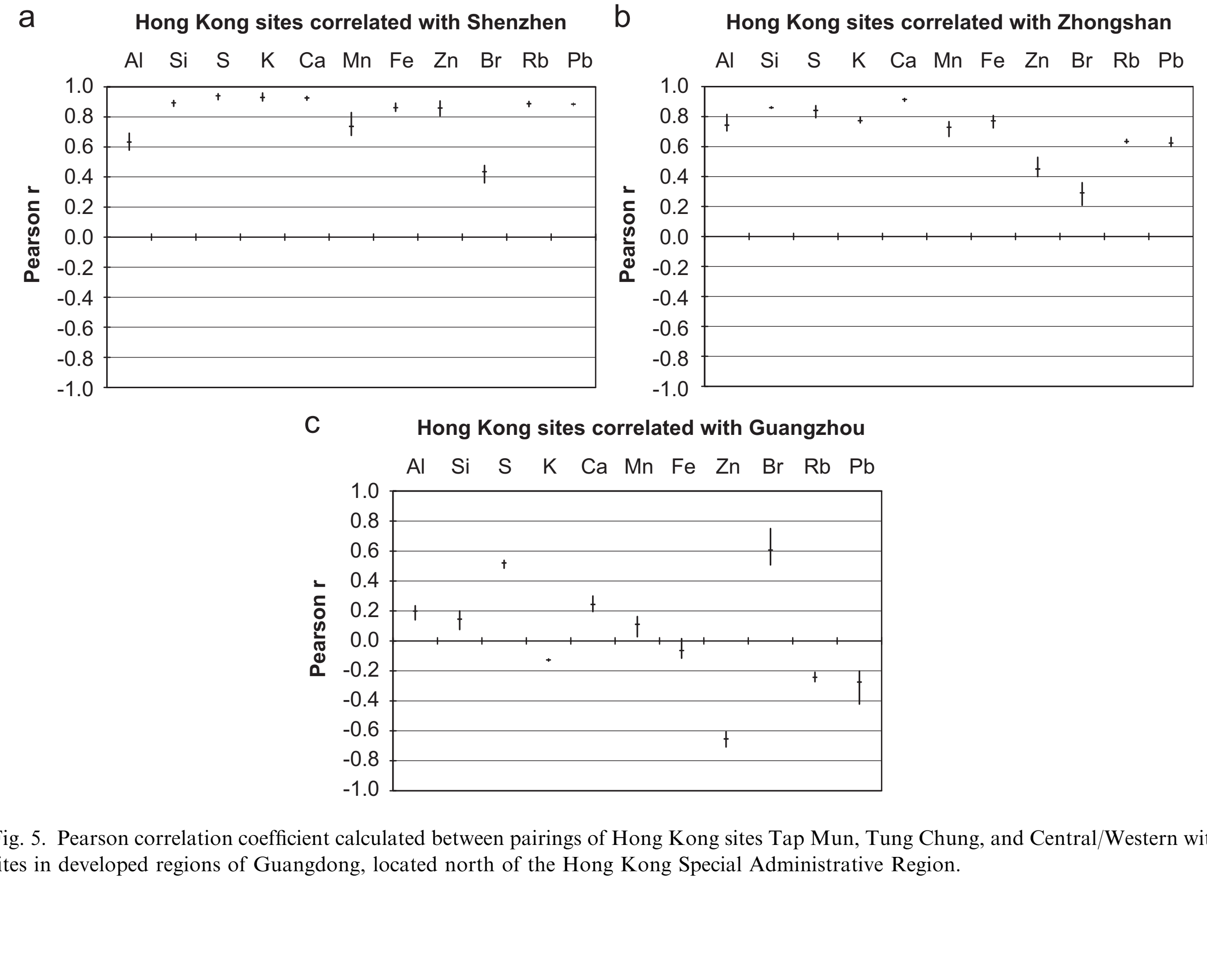

Fig. 5. Pearson correlation coefficient calculated between pairings of Hong Kong sites Tap Mun, Tung Chung, and Central/Western with sites in developed regions of Guangdong, located north of the Hong Kong Special Administrative Region.

relationship (average $r = 0.43$). The pairing of Hong Kong and Zhongshan (Fig. 5b) also has a moderate to strong relationship for nine species (Al, Si, S, K, Ca, Mn, Fe, Rb, and Pb), while Zn and Br stand out for low correlation. Finally, correlating Hong Kong with Guangzhou leads to no correlation for eight species (Al, Si, K, Ca, Mn, Fe, Rb, and Pb), with moderate positive correlation for S and Br, and moderate negative correlation for Zn. The low correlation of the eight species between Hong Kong and Guangzhou combined with the regional maximum average concentration of each species recorded at Guangzhou points to this rapidly industrializing area as a major source area of both crustal material (Al, Si, Ca, and Fe) and anthropogenic species (K, Mn, Rb, and Pb).

The varying relationship of Br and Zn for pairings of Hong Kong sites with Guangzhou, Zhongshan, and Shenzhen points to sources in the Guangdong Province influencing the Hong Kong area. The strong positive correlation of Zn at Shenzhen, no correlation at Zhongshan, and moderately negative correlation at Guangzhou indicates possible source area located south of Guangzhou and near Zhongshan. In addition, the source location of Br is perplexing, having the maximum concentration observed at rural northern site, Conghua, yet also poor correlation for Hong Kong sites paired with Shenzhen and Zhongshan. One previous study linked Hong Kong's bromide levels with vehicular sources and road dust (Lee et al., 1999), although incineration has also been suggested as another potentially important source for the region (Louie et al., 2005a). Clearly, further research is needed to evaluate the source characteristics of Br in the Pearl River Delta. Finally, the moderate to high correlation of S (average Pearson r of 0.52–0.94) between Hong Kong and the three developed sites in Guangdong supports earlier analysis which described region-wide increases in sulfate levels during northerly flow (Hagler et al., 2006), although local sources of S are also expected. Given that sulfate is a significant component of $PM_{2.5}$ throughout the region (Hagler et al., 2006), sources outside of the Pearl River Delta region may be an important factor influencing overall $PM_{2.5}$ concentrations in the area.

3.3. Factor analysis

After having established that all three Hong Kong sites and to a major extent, Shenzhen, are influenced by external sources for 11 species (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb), statistical relationships between these species can point to source types. Combining data for the three Hong Kong sites and Shenzhen, Principal Components Analysis was performed using a statistical software package (SPSS 12.0). Shown in Table 3, two factors were found that represented 81% of the total variance, with one factor displaying crustal characteristics (Al, Si, Ca, and Fe) while the second signifies a mix of urban and industrial activities (K, Mn, Zn, Rb, and Pb). While the former grouping is unsurprising, as Al, Si, Ca, and Fe exhibited similarly low crustal enrichment factors, the latter clustering of elements may not be easily explained as originating from the same source. For example, K is often used as a common tracer for biomass burning (Watson et al., 2001), while Pb has a multitude of non-biomass burning sources including fossil fuel combustion and metallurgy (Nriagu and Pacyna, 1988). A likely explanation for the clustering of these anthropogenic elements is a combination of similar origin and co-located sources at a distance from Hong Kong, resulting in a general anthropogenic pollution signature observed in the Hong Kong area.

Table 3
Principle components analysis of measurements made at sites in Hong Kong (Tap Mun, Tung Chung, Central/Western), and Shenzhen

	Component[a]	
	1	2
Al	.249	**.912**
Si	.456	**.865**
S	.499	.227
K	**.826**	.486
Ca	.315	**.898**
Mn	**.749**	.553
Fe	.562	**.790**
Zn	.895	.323
Br	.462	.429
Rb	**.903**	.301
Pb	**.928**	.303
% Variance	44.3%	37.0%

[a]Rotation method: Varimax with Kaiser normalization.

4. Conclusions

This study seeks to aid regional air quality policy development in the Pearl River Delta Region of

China through retrieving source information from recent ground measurements of $PM_{2.5}$ species. Four months of filter sampling occurred at seven locations in 2002–2003, characterizing 20 samples per site with detailed chemical information (major ions, elements, and carbonaceous species). Region of origin and source type were estimated for 24 elements based upon spatial-variability in concentrations, inter-site correlations, enrichment factors, and principle component analysis.

Overall, our findings suggest that the improvement of air quality in Hong Kong can be largely achieved by reducing emissions in the Pearl River Delta Region, both within Hong Kong and in neighboring Guangdong. Looking specifically at the sites located in Hong Kong, it appears that sources within the city may considerably influence local $PM_{2.5}$ concentrations. Significant differences in concentration among three Hong Kong sites were observed for a number of species (EC, Cl, V, Cr, Co, Cu, Sr, and Sn), which also indicates spatial variability in local population exposure. In addition, low ($r<0.5$) or moderate ($0.5<r<0.8$) inter-site correlation supports the conclusion that Hong Kong is impacted by local sources for the above elements as well as several others (As, Ni, Na, Se, and Tl).

In addition to local sources impacting Hong Kong's $PM_{2.5}$ species, it appears that the heavily developed northern (Guangdong) section of the Pearl River Delta substantially influences regional air quality. With elements initially grouped by their enrichment factors as primarily crustal, oceanic, or anthropogenic origin, it was found that Guangdong sites had generally much higher concentrations of both crustal and anthropogenic elements in relation to sites in Hong Kong. In addition, the high inter-site correlation ($r>0.8$) of certain elements (Al, Si, S, K, Ca, Mn, Fe, Zn, Br, Rb, and Pb) and their similar magnitude of concentration throughout Hong Kong points to region-wide impacts by sources external to the city. This subgroup of elements were studied using Principal Components Analysis and nine were found to group as a crustal identity (Al, Si, Ca, and Fe) and an anthropogenic pollution signature (K, Mn, Zn, Rb, and Pb) potentially linked by co-located industrial activities, such as biomass burning and incinerator emissions. Correlative analysis extended to include source areas in Guangdong suggests that Guangzhou is a regionally important source area of crustal species and anthropogenic elements (K, Mn, Rb, and Pb), with Zn appearing to be controlled by a source area between Guangzhou and Zhongshan. Finally, the moderate to high inter-site correlation of S in all analyses supports the influence of long-distance transport into the Pearl River Delta, although local sources are also expected to contribute to regional concentrations.

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