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Developing chemical signatures of particulate air pollution in the Pearl River Delta region, China

Mei Zheng[1,2], Yuan Cheng[2], Limin Zeng[1], Yuanhang Zhang[1,*]

1. College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China. E-mail: mzheng@pku.edu.cn
2. School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA

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Abstract

$PM_{2.5}$ samples were collected in a regional sampling network with three sites in Hong Kong and four sites in the adjacent inland Pearl River Delta (PRD) or Guangdong Province during four months/seasons from 2002–2003. Trans-boundary transport between Hong Kong and the inland PRD is inevitable under the influence of Asian monsoon. In summer, Hong Kong serves as the upwind site of the inland PRD while during other seasons it is under the influence of continental emissions. Previous studies have recognized the importance of using chemical signatures to differentiate local vs. regional contributions to air pollutants in Hong Kong such as the CO/NOx ratio, ratios of different VOC species. In this study, detailed chemical speciation by gas chromatography-mass spectrometry was performed with $PM_{2.5}$ samples to identify new chemical signatures to distinguish aerosols in Hong Kong from those from the inland PRD. Since Hong Kong is not influenced by the continental emissions from the inland PRD during summer, comparison focused on chemical data obtained from this season for chemical signatures. The new ratios developed from the current study include LCPI/HCPI ratio of alkanes (0.39 ± 0.02 in Hong Kong vs. 0.78 ± 0.08 in the inland PRD), pyrene to benzo[ghi]perylene ratio (0.97 ± 0.21 in Hong Kong compared to 0.20 ± 0.06 in the inland PRD), and the ratio of 1,2-benzenedioic acid to 1,4-benzenedioic acid (1.8 ± 0.1 in Hong Kong vs. 0.6 ± 0.05 in the inland PRD). Results from this study also revealed that Hong Kong was impacted by ship emissions as reflected by substantially high V/Ni ratio (9 ± 2) while this ratio was about 1–2 at all sites in the inland PRD, which is very close to typical ratios from residual oil combustion.

Key words: $PM_{2.5}$; chemical signature; local and regional air pollution; Hong Kong; Pearl River Delta

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Introduction

During the past two decades, China has experienced amazing economic and population growth as well as rapid expansion of urbanization and industrialization. However, because of the same reasons, China is facing serious challenge of various air pollution problems today. For example, air quality of almost 70% of cities did not meet the national air quality standards according to the data from air quality monitoring network in 360 cities in 2004 (Shao et al., 2006). Although the sources of air pollution vary from city to city, there are also some common origins and issues, e.g., coal is still the major energy source in China and air pollution in China today is characterized by coal emissions mixed with vehicular exhaust in most urban areas. In Beijing, the number of vehicles in 2002 is 2 million, an increase by a factor of 4 compared to only 0.5 million in 1990 (Tang, 2005). With much higher emission factors than developed countries, air pollution from vehicular emissions gets even worse in China.

The inland Pearl River Delta (PRD) in Guangdong province, located in southern part of China and adjacent to Hong Kong, is one of the three major developed zones in China. It is a highly urbanized region, and economically very important as it accounts for 19% of total gross domestic product (GDP) in China. There is a rapid increase in air quality research in the inland PRD and Hong Kong as can be seen by the increased publications in recent years (Chan and Yao, 2008). Hong Kong is surrounded by South China Sea on the east and south, Pearl River Estuary on the west and the inland PRD on the north, and bordered with Shenzhen, one of the two megacities (Guangzhou as another one) in the inland PRD. The landscape of Hong Kong is fairly hilly to mountainous with steep slopes. Under the climate system associated with the Asian monsoon, the prevailing wind direction exhibits distinct seasonal variations and thus the trans-boundary transport between Hong Kong and the inland PRD is inevitable due to the alternations of the dominant air masses in Hong Kong (oceanic in summer vs. continental in winter).

* Corresponding author. E-mail: yhzhang@pku.edu.cn

Air quality deteriorates in a fast pace in this region no matter how one chooses to measure it. A simple example is the increase of the number of haze days in the region. Recognizing the urgent need for air pollution abatement, studies have been undertaken in order to identify sources of air pollutants especially the local/regional signatures of pollution sources in Hong Kong. The Hong Kong and Guangdong Governments have started to take individual and joint efforts for reducing regional air pollution. A better understanding of the local and regional signatures in Hong Kong aerosols is critical to formulate effective control strategies. Several signatures have been developed previously in various studies and are briefly summarized here.

(1) SO_2/NOx and CO/NOx ratios: the air masses from continent or the inland PRD were characterized by relatively high concentration of CO and SO_2, while the air masses in Hong Kong by high NOx concentration. Hong Kong is very hilly with only 25% of land developed, requiring heavy-duty buses as one of the major transportation means. Roadside emissions are threatening human health in Hong Kong since almost half of the its population live a few minutes away from heavy traffic with congested roads and high-rise buildings preventing active dispersion of pollutants. Thus, the ratio of SO_2 to NOx and the ratio of CO to NOx can provide signatures of the air masses from Hong Kong and the inland PRD. The SO_2/NOx and CO/NOx ratios at the inland PRD were much higher since it is one of the famous manufactory and industrial centers in the world. For example, the SO_2/NOx ratio was found to be 1.26 at a site in the inland PRD and 0.25 in Hong Kong (Guo et al., 2009). An airborne study around Hong Kong Territory during October and November 1994 indicated poor air quality on the west and north sides of Hong Kong with a CO/NOx ratio as high as 10, similar to those found in the upwind mainland China (Kok et al., 1997). Wang et al. (2003) suggested that Hong Kong plumes typically have a CO/NOx ratio of 3.9–6 whereas air masses from mainland China contain a much higher ratio (~20). Recently, Guo et al. (2009) reported a CO/NOx ratio of 52.0 and 15.8 in the inland PRD and Hong Kong, respectively.

(2) Volatile organic carbon ratios: the ratio of a more reactive volatile organic carbon (VOC) to a less reactive VOC could provide useful information about the atmospheric processes of air masses, including atmospheric transport and photochemical aging. A higher ratio indicates relatively little photochemical processing of the air mass which is more likely from local origin, whereas a lower ratio indicates more aged VOCs and thus the VOCs are more likely emitted from more distant sources (Guo et al., 2009). Guo et al. (2009) compared the ratios of *m*, *p*-xylene/ethylbenzene and *i*-butane/propane at Hong Kong and the inland PRD since the lifetime of *m*, *p*-xylene and ethylbenzene, *i*-butane, and propane is 1, 2, 6, and 12 days, respectively. During their study period, both VOC ratios were higher in Hong Kong, indicating the importance of local and fresh emissions.

The ratio of VOC species with similar photochemical lifetimes can be used to estimate the relative importance of different source types to the VOCs observed at a given site. Zhang et al. (2008) compared the ratio of hexane to toluene in Hong Kong and the inland PRD, which have lifetimes of about 2 days. The ratio was relatively low at Guangdong Province, indicating the presence of abundant toluene and thus the significant contribution from industrial sources.

(3) Chlordane ratio: Li et al. (2007) found the ratio of *trans*-chlordane (*t*-CHL) to *cis*-chlordane (*c*-CHL) at Hong Kong and Guangzhou (the capital city in Guangdong province) were significantly different, averaging 0.95 and 0.78, respectively. The *t*-CHL/*c*-CHL ratio of Guangzhou was comparable with that of commercially available technical chlordane in Guangzhou market (0.76).

(4) Indication by spatial variations: distributions of air pollutants in different sites have been frequently studied in Hong Kong, which have been used to assess the impact of regional air pollution. A reduction in $PM_{2.5}$ mass concentration at the roadside in Hong Kong (ca. 9%), which was attributed to the decrease of carbonaceous components, was observed during 2000 and 2004 (So et al., 2007), indicating the effective control of motor vehicle emissions. However, $PM_{2.5}$ concentration was found to increase during the same period at the urban and rural sites (15%–20%), indicating the increasing impact of regional air pollution. Significant difference in concentration among sampling sites in Hong Kong was observed for a number of species of $PM_{2.5}$, such as EC, V, Cr, Co, Cu, Sr, and Sn, indicating the dominance of local sources (Hagler et al., 2007). In contrast, high inter-site correlations of several species, such as sulfate, Si, Al, Ca and Fe, were observed, and similar magnitude was also found throughout Hong Kong, suggesting regional impacts by sources from the inland PRD (Hagler et al., 2007; So et al., 2007).

(5) Indication by seasonal variations: the Asian monsoon is the dominant meteorological feature of this region, enhancing the regional transport of pollutants. As a result, the seasonal patterns of species of $PM_{2.5}$ could be used to estimate the relative importance of local and regional contributions. This is because species from regional source exhibit more pronounced seasonal variation in Hong Kong. For example, $PM_{2.5}$ in Hong Kong was found highest in winter mainly due to the elevated organic carbon (Louie et al., 2005), and contribution of emissions from Guangdong Province (the inland PRD) was estimated to be significant (Hagler et al., 2006). EC in Hong Kong showed limited seasonal variability, indicating the dominance and strength of emissions from local mobile sources (Louie et al., 2005).

More chemical signatures can certainly help to better distinguish local emissions from regional impacts in Hong Kong. This is a first program in this region, which allows simultaneous measurements at three sites in Hong Kong and four sites in Guangdong Province for four months during one year. More importantly, compared to previous studies, this study provides detailed information of organic composition of aerosols through gas chromatography-mass spectrometry (GC-MS) analysis. The same sampling strategy as well as analytical protocols makes a direct

comparison of $PM_{2.5}$ compositions and sources between Hong Kong and the inland PRD possible. Therefore, this study aims to develop new chemical signatures of aerosols especially organic species in Hong Kong and the inland PRD through the simultaneous aerosol sampling and by taking advantage of measurements of more species/pollutants than previous campaigns.

1 Materials and methods

Sampling of ambient $PM_{2.5}$ samples have been described by Hagler et al. (2006). For every six day in each of the following four months (December 2002, March 2003, June 2003, and October 2002), 24-hr $PM_{2.5}$ samples for organic speciation analysis were collected on quartz fiber filters installed in one of the four parallel channels through a cyclone-based size selection at a flow rate of 16.7 L/min. Samples for trace metal analysis by X-ray fluorescence (XRF) were collected in another channel on Teflon filter. As can be seen from Fig. 1, samples were collected from three sites in Hong Kong including Tap Mun (TM), Tung Chung (TC), and Central and Western (CW) and four sites in the inland PRD (Zhongshan (ZS), Shenzhen (SZ), Conghua (CH), and Guangzhou (GZ)).

Samples for elemental analysis including V and Ni were performed on individual filters by Desert Research Institute using XRF. However, samples on the prebaked quartz fiber filters of the same month at each site were combined as a monthly composite prior to organic speciation analysis in order to achieve enough mass for the analysis by GC-MS. The experimental procedure has been well described elsewhere (Zheng et al., 2002). Briefly, a mixture of 16 deuterated internal standards (IS) was spiked in each sample before extraction. Each sample was ultrasonically extracted with hexane (twice) and a mixture of benzene and isopropanol (2:1) (three times). The extract was filtered, combined, and reduced to about 5 mL by a rotary evaporator, and then further blown down by ultrapure nitrogen. The final extract was derivatized by diazomethane in order to convert the organic acids to their methyl ester analogues. Then the target organic species in the derivatized extracts were identified and quantified by GC-MS on a Hewlett-Packard 6890 GC equipped with a Hewlett-Packard 5973 Network mass selective detector using a 30 m × 0.25 mm × 0.25 μm film thickness HP-5 MS capillary column. A set of quantification standards containing more than one hundred standard compounds was provided to assist in the identification of target compounds.

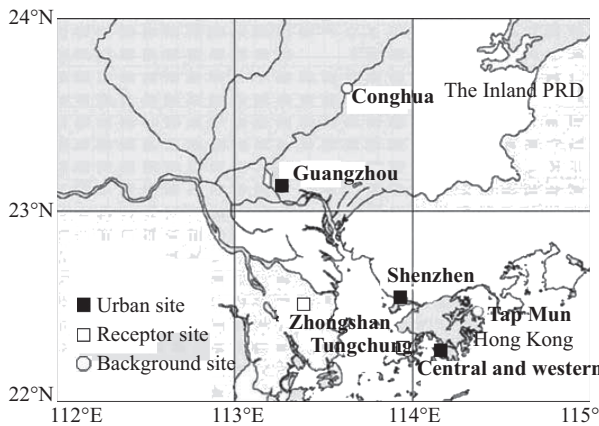

Fig. 1 Sampling sites including four sites in the inland PRD (Conghua, Guangzhou, Zhongshan, and Shenzhen) and three sites in Hong Kong (Tap Mun, Tung Chung, and Central and Western). The receptor sites are set to monitor emissions of urban plumes such as Guangzhou.

2 Results and discussion

2.1 Ratio of alkane CPI as signature

Table 1 summarizes solvent extractable organic compounds identified in this study as well as ratios of various species. Among all the seven sites, the highest alkane concentration was measured in Guangzhou, except for the fall sample at ZS (120.6 ng/m^3). The summed concentration of alkanes from C_{17}–C_{35} ranged from 18.9 to 41.9 ng/m^3 in Hong Kong and from 16.2 to 142.2 ng/m^3 in the inland PRD. Distinct lower levels in summer were found in both Hong Kong and the inland PRD, resulting in a wide range of total alkane concentrations. But abundant alkanes were still found in Guangzhou in summer (67.6 ng/m^3 compared to only 5.2 ng/m^3 in TM), suggesting Guangzhou was still an active source of alkanes even though in summer. Alkanes in the atmosphere are mainly from high plant wax and petroleum residues. Our analysis indicated that about 81% of alkanes during summer in Guangzhou (GZ) was from petroleum residues although it was only about 60% in Hong Kong. This confirms the importance of primary and anthropogenic emissions in Guangzhou. The increased importance of petroleum residues in winter was clear with pertroleum residue contribution higher than 70% at all sites (Table 1). In Hong Kong, what is higher in summer was carbon preference index (CPI, about 2), implying the importance of vegetative detritus. The carbon number maximum (C_{max}) was dominated by C_{29} or C_{31} in summer, while C_{25} was the most abundant alkane in several samples in spring.

The CPI of alkanes (defined as the sum of the odd carbon number homologues divided by the even carbon number homologues) can be divided into two subsets: low carbon preference index (LCPI, C_{17}–C_{26}), primarily from combustion sources, and high carbon preference index (HCPI, C_{27}–C_{36}), mainly derived from vegetative detritus with clear odd carbon dominance such as C_{29}, C_{31}, and C_{33}. Previous studies have shown that CPI can be used to discriminate between biogenic and fossil fuel contributions of alkanes with biogenic sources having higher CPI values and fossil fuel residues showing no carbon number preference (CPI value of unity) (Simoneit and Mazurek, 1982). Figure 2 illustrates the ratios of LCPI to HCPI of HK and GD samples in different seasons.

Based on the meteorological analysis from Hagler et al. (2006), during the sampling period the prevailing wind in summer was clearly from South and Southwest and Hong Kong was not impacted by air pollutants from sites in the inland PRD. Thus, the difference of aerosol characteristics

Table 1 Concentrations (ng/m^3) and ratios of organic species in Hong Kong and the inland PRD samples

Site-Month	Sum of alkane	CPI of alkane	C_{max} of alkane	Percentage from petroleum (alkane)	Sum of PAHs	PYR/ BghiP	FLU/ (FLU+ PYR)	INP/ (INP+ BghiP)	Aliphatic diacids	Aromatic diacids	Ratio of 1,2-/ 1,4-benzene-dioic acid
TM-03	15.78	1.6	C31	76	5.30	0.77	0.51	0.53	46.81	14.02	1.1
TC-03	31.75	1.3	C25	85	8.40	0.69	0.47	0.50	21.76	8.56	1.0
CW-03	33.55	1.5	C25	78	6.08	0.83	0.49	0.47	36.60	13.65	1.0
CH-03	74.03	2.2	C31	60	27.31	0.59	0.50	0.51	72.88	34.10	0.9
ZS-03	66.64	1.2	C25	87	30.31	0.33	0.45	0.50	36.85	67.75	0.5
SZ-03	59.21	1.3	C25	84	26.14	0.27	0.46	0.49	30.40	18.98	0.3
GZ-03	118.79	1.4	C31	81	40.32	0.26	0.46	0.47	69.31	34.14	0.5
TM-06	5.17	2.0	C29	62	0.63	0.67	0.56	0.50	7.41	2.78	1.9
TC-06	8.34	2.1	C29	58	1.06	1.13	0.50	0.50	10.41	3.80	1.7
CW-06	10.44	2.1	C31	57	1.20	1.11	0.50	0.47	7.95	2.93	1.1
CH-06	18.18	1.9	C31	67	6.09	0.26	0.48	0.47	17.89	9.81	0.7
ZS-06	16.40	1.4	C29	79	4.68	0.25	0.43	0.51	6.70	5.45	0.6
SZ-06	18.82	1.7	C23	69	6.23	0.15	0.50	0.49	12.39	4.93	0.6
GZ-06	67.62	1.4	C31	81	18.63	0.12	0.47	0.46	29.62	17.34	0.5
TM-10	20.84	1.8	C31	71	5.51	0.75	0.49	0.55	28.51	9.90	1.0
TC-10	25.43	1.9	C31	68	7.99	0.50	0.49	0.52	32.39	14.92	0.8
CW-10	25.52	1.9	C31	67	5.16	0.72	0.51	0.49	30.59	9.99	0.9
CH-10	37.15	1.7	C31	72	11.60	0.39	0.49	0.49	46.10	11.58	1.2
ZS-10	120.56	1.2	C25	88	61.26	0.24	0.45	0.50	42.53	41.89	0.9
SZ-10	58.58	1.4	C31	81	28.29	0.25	0.45	0.50	46.47	27.32	0.3
GZ-10	94.01	1.5	C31	76	38.03	0.19	0.46	0.47	50.88	39.17	0.4
TM-12	18.93	1.8	C31	73	6.39	0.80	0.51	0.53	46.45	19.35	1.5
TC-12	41.94	1.3	C25	82	9.39	0.55	0.50	0.49	37.11	17.48	1.4
CW-12	35.79	1.6	C31	72	7.83	0.77	0.48	0.49	44.54	19.29	1.3
CH-12	32.41	1.8	C31	70	24.36	0.32	0.48	0.47	36.21	14.20	1.3
ZS-12	68.24	1.2	C26	84	27.44	0.26	0.47	0.49	42.96	32.30	0.8
SZ-12	59.67	1.3	C31	82	30.79	0.31	0.46	0.50	45.07	23.32	0.7
GZ-12	142.19	1.4	C25	81	55.28	0.19	0.46	0.46	46.38	39.67	0.3

CPI: carbon preference index; Cmax: carbon number maximum. Sampling sites: Hong Kong including TM, TC, CW; Guangdong including CH, ZS, SZ, GZ.

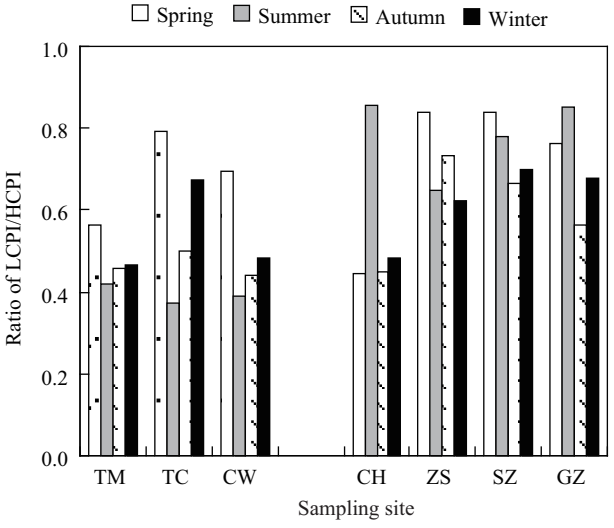

Fig. 2 LCPI (low carbon preference index) to HCPI (high carbon preference index) ratio of alkanes including three sites in Hong Kong (TM, TC, and CW) and four sites in the inland PRD (CH, ZS, SZ, and GZ).

between Hong Kong and the inland PRD can be achieved through the analysis of summer data. In another word, the characteristics of air pollutants in Hong Kong in summer are more representative of local sources of Hong Kong. During other seasons, Hagler et al. (2006) found most of the time Hong Kong became a downwind site, thus Hong Kong was influenced by the air masses from the inland PRD. When alkane CPI in summer was examined, lower LCPI/HCPI ratio was found in Hong Kong (0.39 ± 0.02), almost half of the average in the inland PRD (0.78 ± 0.08) (Fig. 2). This suggests that a higher biogenic contribution of alkanes to aerosols in Hong Kong especially in summer, compared to the inland PRD.

2.2 Ratio of PAH as signature

PAHs are produced by fuel burning including fossil fuel (e.g., oil and coal) and biomass. The most concern for PAHs is their toxic effect, which depends on molecular size and shape and other structural features, and has a wide range from being nontoxic to extremely toxic. Most of the PAHs included in this study are known for their carcinogenic and mutagenic properties such as benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[ghi] perylene (BghiP), coronene, indeno[1,2,3-cd]pyrene (INP).

The sum of individual PAHs in $PM_{2.5}$ samples is shown in Table 1. The total PAH concentration ranged from 0.24 to 9.39 ng/m^3 in Hong Kong and from 4.68 to 61.26 ng/m^3 in the inland PRD. The average PAH concentration in the inland PRD (24.58 ng/m^3) was five times the average in Hong Kong (4.53 ng/m^3). It is interesting to note that PAH concentration exhibited very small spatial variations while in the inland PRD the total PAH concentration varied greatly from site to site. For example, the average concentration in fall and winter in Hong Kong was (6.22 ± 1.26) ng/m^3 and (7.87 ± 1.23) ng/m^3, respectively, while in the inland PRD the fall average was (34.80 ± 17.97) ng/m^3 and the winter average was (34.47 ± 12.23) ng/m^3. At all

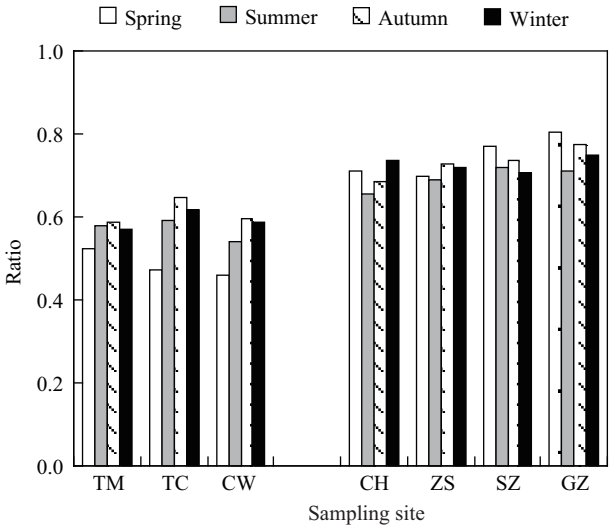

Fig. 3 Ratio of PAH with molecular weight equal to or above 252 in total PAHs during each season. TM, TC and CW are sites from Hong Kong and all other sites are from the inland PRD.

sites, the lowest concentration of total PAHs was found in summer ((0.96 ± 0.24) ng/m^3 in Hong Kong and (8.91 ± 5.65) ng/m^3 in the inland PRD).

Pyrogenic PAHs from combustion sources and petrogenic PAHs from petroleum inputs are two primary sources of PAHs in the environment. Ratios like fluoranthene/(fluoranthene+pyrene) (FLUO/(FLUO+PYR)) and INP/(INP+BghiP) have been widely used to identify the sources of PAHs in rivers, estuaries, and marine sediments. Petrogenic source is characterized by a FLUO/(FLUO+PYR) ratio of < 0.2 and a INP/(INP+BghiP) ratio of < 0.2, however, a ratio > 0.5 for both indexes suggests combustion sources from coal, wood or grass, etc. (Yunker et al., 2002). As can be seen from Table 1, the ratios in all samples were close or higher than 0.5, suggesting that combustion source or pyrogenic source was the major pathway for PAHs measured in the atmosphere of both Hong Kong and the inland PRD.

The split between light and heavy PAHs showed difference. PAHs in the inland PRD were characterized by the enrichment of heavier PAHs with molecular weight ⩾252 PAH accounting for about 72% of total PAHs in summer and this was consistently seen in all seasons (Fig. 3). For Hong Kong, the percentages of ⩾ 252 PAHs were as low as 47% at TC and 46% at CW, indicating PAHs from local source in Hong Kong was characterized by lighter PAHs. In seasons other than summer, this percentage in Hong Kong increased, reflecting the influence from PAHs from the inland PRD.

This enrichment of heavier PAHs in the inland PRD can be clearly reflected by the ratio of lighter to heavier PAHs. When the pyrene to benzo[ghi]perylene ratio (PYR/BghiP) was examined, higher ratio was always found in Hong Kong ((0.76 ± 0.05) vs. (0.36 ± 0.13) in spring, (0.97 ± 0.21) vs. (0.20 ± 0.06) in summer, (0.66 ± 0.11) vs. (0.27 ± 0.07) in fall, and (0.71 ± 0.11) vs. (0.27 ± 0.05) in winter). The highest contrast was seen in summer with PYR/BghiP ratio as 0.97 in Hong Kong and 0.20 in the inland PRD.

2.3 Ratio of aromatic diacids as signature

Three aromatic diacids were investigated in this study, namely 1,2-benzenedioic acid, 1,4-benzenedioic acid, and 1,3-benzenedioic acid. The first two account for 95% of the sum of these three aromatic diacids. The difference between Hong Kong and Guangzhou can be seen from the ratio of 1,2-benzenedioic acid to 1,4-benzenedioic acid with a ratio > 0.8 in all Hong Kong samples and < 0.5 in Guangzhou, the capital city of Guangdong Province (Table 1). This ratio at the rural CH site was consistently higher than those at other urban sites in the inland PRD. This implies that 1,4-benzenedioic acid is a better indicator for anthropogenic urban emissions than other aromatic diacids. The ratio of 1,2-benzenedioic acid to 1,4-benzenedioic acid at the urban areas in Hong Kong during summer was 1.8 ± 0.1 while it was 0.6 ± 0.05 at the urban sites in the inland PRD.

However, aliphatic diacids exhibit very different patterns compared to aromatic acids. Although aliphatic diacids is similar as other species in that the lowest level was measured in summer (8.59 ng/m^3 in Hong Kong, and 16.65 ng/m^3 in the inland PRD) except for the spring samples, very little spatial variation was seen especially in the winter samples when aliphatic acids were evenly distributed among the seven sites in the PRD (42.7 ± 4.0) ng/m^3 in Hong Kong and (42.7 ± 3.9) ng/m^3 in the inland PRD). Such a homogenous distribution is just like sulfate, a known component formed secondarily and behaved as a regional background. Not only the concentration or level was evenly distributed among sites, but also the distribution patterns of aliphatic diacids in each sample with propanedioic acid accounting for ca. 40% of total aliphatic diacids and butanedioic acid for ca. 30%. Since aliphatic diacids were not detected in major primary emission source tests, our results provided supportive evidence that secondary formation is most likely their major source in the atmosphere.

2.4 Ratio of vanadium to nickel as signature

Unlike other species, the measured V concentration was significantly higher at the urban CW site in Hong Kong, a level much higher than those found in the inland PRD (Fig. 4a). But it was still lower at another two sites in Hong Kong. This high level of V at CW was found at all four seasons (as abundant as 9.6% ± 1.6% in $PM_{2.5}$). V and Ni are traditional tracers of residual oil combustion (Pacyna et al., 1984; Isakson et al., 2001), however Ni surprisingly did not show the same pattern as V (Fig. 4b). Instead, the percentage of Ni in $PM_{2.5}$ was about the same at all three sites in Hong Kong at all seasons (1.3% ± 0.4% in $PM_{2.5}$). Thus, the V/Ni ratio was extremely high at CW, ranging from 7–11 with a ratio of 10 in summer. This ratio was only 1.7±1.0 in the inland PRD in summer. The data from several residual oil source (including boiler and power plant) test results from US EPA SPECIATE 3.2 database show that V/Ni ratios range from 0.47–2.26 with an average of 0.95. This suggests that V and Ni in the inland PRD were mainly from the combustion of residual

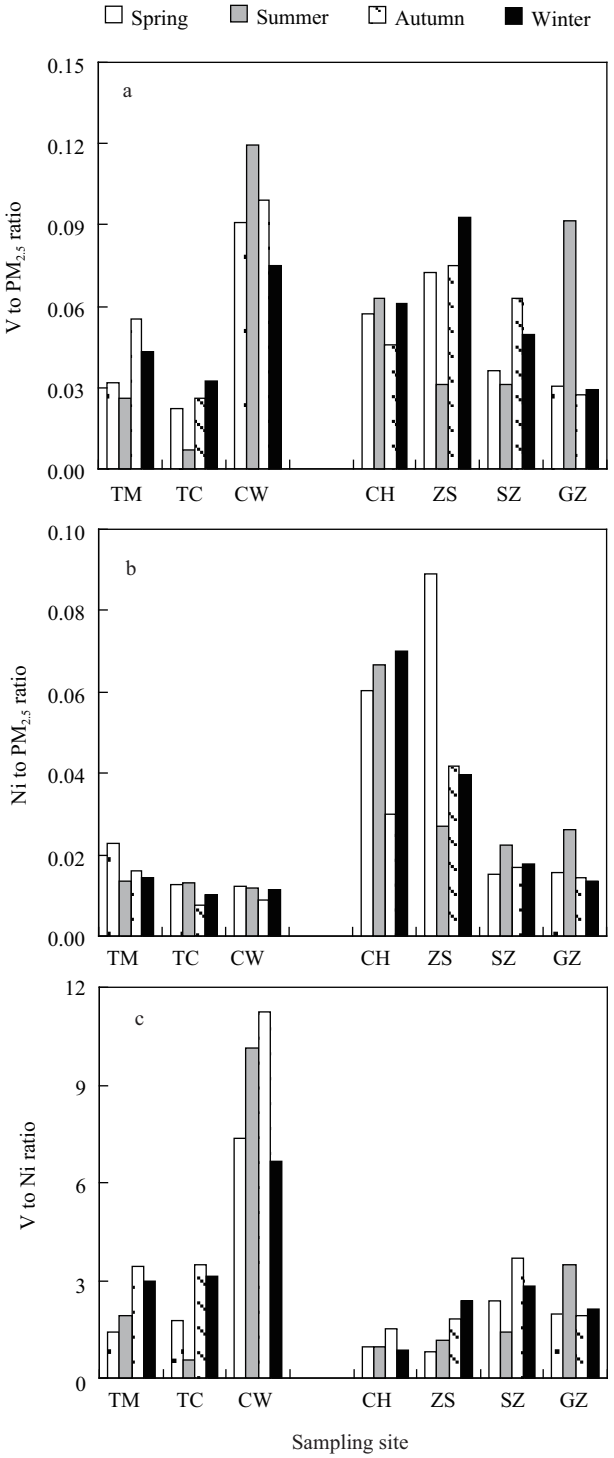

Fig. 4 The abundance of V (a) and Ni (b) in $PM_{2.5}$ and V/Ni ratios (c) in three sites in Hong Kong and four sites from the inland PRD during each season.

oil used in industry operations, but obviously it was not the case for the CW site in Hong Kong.

A recent study in an important harbor, Melilla, Spain examined the shipping emission characteristics in a Mediterranean city and found the commercial shipping emissions had a V/Ni ratio as 4–5, much higher than the ratios from residual oil combustion from power plants and boilers (Viana et al., 2009). As the CW site is very close to the Victoria Harbor, which is one of the busiest ports in the world, the significant high V/Ni ratio at CW (9 ± 2) reflects the shipping emissions characteristics in Hong Kong.

There is an increasing concern of the impact of shipping emissions on air quality in Hong Kong in recent years as many ships, mainly container tankers, load and unload cargos everyday. In 2006, the volume handled by the Hong Kong and Shenzhen's port together accounts for 9.5% of the world's container throughput, much higher than other major coastal ports such as Shanghai (4.9%) and Singapore (5.6%) (Galbraith et al., 2008), which are three of the world's five busiest ports. Unfortunately, the highest population density in Hong Kong is along the Victoria Harbor, meaning a large number of residents in Hong Kong could be directly or indirectly exposed to ship emissions. Lack et al. (2009) identified that particulate matter from commercial shipping is composed of 46% sulfate, 39% organic matter, and 15% black carbon. The model estimate of mortality due to global shipping traffic suggests that the number of people dying from heart and lung disease as a result of under-regulated shipping emissions is 60,000 in 2002 (Corbett et al., 2007). The assessment of air pollutants from ship emissions and health impacts should be included in future research in this region. This study revealed that the site in Hong Kong close to the harbor had its distinctive V/Ni ratio, a ratio much higher than those found in the inland PRD.

3 Conclusions

Summer is the season when the prevailing wind is from the sea and Hong Kong is not under the influence of air masses from the inland PRD, thus aerosols in Hong Kong exhibit local characteristics. Simultaneous sampling at Hong Kong and the inland PRD allow the identification of new chemical signatures to differentiate air masses from local or the inland PRD in Hong Kong. Significantly higher organic pollutant levels were found in the inland PRD as it accounts for more than 90% of particulate matter emission in this region. More petroleum-derived alkanes were found in the inland PRD while Hong Kong had abundant vegetative-derived alkanes, resulting in lower LCPI/HCPI ratios in Hong Kong. Combustion-derived PAHs dominated in this region. However, heavier PAHs (MW $\geqslant$ 252) was enriched in the inland PRD. This difference can be seen from the PYR/BghiP ratio (0.97 in Hong Kong compared to 0.20 in the inland PRD). The presence of abundant 1,4-benzenedioic acid was also found in the inland PRD samples and the ratio of 1,2-benzenedioic acid to 1,4-benzenedioic acid can reflect the difference. The V/Ni ratio was identified as a signature that distinguished aerosols in Hong Kong from those in the inland PRD, which was significantly higher at CW, a site close to Victoria Harbor. This ratio was close to 10 in summer while it was only 1.7±1.0 in the inland PRD, indicating the influence of ship emissions on Hong Kong air quality, and the contribution of residual oil combustion in the inland PRD. From this study with simultaneous sampling and same analytical protocols for $PM_{2.5}$ samples in Hong Kong and the inland PRD, new chemical signatures were developed to differentiate respective air masses,

in a hope to assist the future study regarding sources of particulate matter in this region especially during episodes when pollutant concentrations reach substantial high levels and threat public health.

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