An Upwind/Downwind Comparative Study of the Solvent Extractable Organic Compounds in PM$_{2.5}$ in Hong Kong

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Abstract

Seven sets of samples that were taken from sites upwind and downwind of Hong Kong during the summer and winter seasons were analyzed. The solvent extractable organic compounds (SEOC) were separated into four major fractions (*n*-alkanes, fatty acids, alkanols and (polycyclic aromatic hydrocarbons [PAHs]) and identified using gas chromatography-mass spectrometry (GC-MS).

Five different wind directions were detected during the two seasons: southwest, southeast, east, east-northeast and northeast. At one extreme, the southwest wind brought clean aerosols from the South China Sea to Hong Kong, diluting the urban aerosols, and the anthropogenic contribution was found to be fresh and local. At the other extreme, when the northeast wind prevailed, there was a significant increase (10-14 times) in the total SEOC yield and the characteristics of the aerosols indicated a greater impact from outside Hong Kong (i.e., more PAHs, plant wax contribution, and lower $C_{18:1}/C_{18:0}$ ratios), suggesting the presence of aged aerosols. In the samples taken during prevailing east-northeast winds in November, the loading was low and bore resemblance to the summer samples. In addition, there were changes in the characteristics of the aerosols, such as an increased plant wax contribution in the fatty acid and alkanol fractions, signifying a change in season. The characteristics and loading of the PM2.5 at the downwind site were found to be significantly influenced by the accumulation of locally emitted air pollutants due to no wind conditions and the transport of long-distance (from surrounding regions) and short-distance (within Hong Kong) plumes.

Keywords: aerosol, PM$_{2.5}$, solvent-extractable organic compounds, transport, Hong Kong.

1. Introduction

The meteorology of coastal cities is influenced by the thermal properties of the landmass and the

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surrounding waters. This thermal condition together with the general atmospheric condition, including seasonal winds, can impact the dispersion of air pollutants. Hong Kong is such a city. It is surrounded by the South China Sea to the east and south (Figure 1), the Pearl River Estuary to the west, and a landmass with complex terrain to the north. The Pearl River water temperature, determined from National Oceanic and Atmospheric Administration (NOAA) satellite imagery, is several degrees different from that of the South China Sea. The summer winds bring clean oceanic aerosols to Hong Kong while polluted air mass from the mainland moves in on the northeasterly winds in the winter (See Figure 1). The prevailing wind in Hong Kong is east to northeasterly.

Figure 1. Sampling sites. HKIA – Hong Kong International Airport.

Hong Kong is one of the most densely populated cities in the world. Its population is concentrated in the Kowloon Peninsula and the northern areas of Hong Kong Island. In recent years, the population in the newly developed areas of the countryside has increased rapidly. The air pollution sources related to population, such as traffic emissions, are also congregated in these regions. In addition, Shenzhen, a city just north of Kowloon in the Mainland, is experiencing economic and urban growth at a very rapid pace. Shenzhen can also contribute to the air pollution in the northern part of Hong Kong. The geographic, meteorological, and demographic conditions in Hong Kong all contribute to the transport of air pollutants within the area.

The solvent extractable organic compounds (SEOC) in total suspended particulate (TSP) and $PM_{2.5}$ (particulate matter of less than 2.5 µm in diameter) of Hong Kong have been characterized by Zheng et al. (1997), Zheng and Fang (2000), and Zheng et al. (2000). The results indicated that vehicular emission was the characteristic of Hong Kong's TSP and $PM_{2.5}$ aerosols, especially in the city. But the transport of aerosols within Hong Kong caused by seasonal winds is still unknown. This study used seven sets of monthly event-by-event upwind/downwind $PM_{2.5}$ aerosol samples, taken

during the summer and winter of 1999-2000, to illustrate the dispersion–and thus the accumulation–of air pollutants in Hong Kong under easterly and northerly winds.

2. Experimental

2.1 Study Sites

The downwind site selected for this study, Tung Chung, is on the west side of Lantau Island just south of the Hong Kong International Airport (HKIA, Figure 1). The airport was commissioned on 6 July 1998 and operates 24 hours a day. Before the building of the new airport, Lantau Island was only sparsely populated with very little traffic and almost no industry.

The upwind sampling site for prevailing easterly winds (summer) was Hong Kong University of Science and Technology (HKUST) located on the west slope of Port Shelter in the countryside of Hong Kong. Previous studies (Zheng et al., 2000) indicate that the composition and loading of the aerosols at this sampling location have a strongly seasonal variation.

Yuen Long is located in the northwest corner of Kowloon and is surrounded by hills with an opening on the northwest side facing Shenzhen across the Maipo Wetland. Both Yuen Long and Shenzhen are rapidly developing townships with manufacturing plants. Furthermore, Yuen Long is near the border crossing-point for Hong Kong and Shenzhen, and is therefore under the influence of heavy-duty vehicles (mostly diesel-powered). The two cities share the same airshed. According to 1995-98 Hong Kong Environmental Protection Department (HKEPD) data (Air Services Group, 1995-98), Yuen Long had the highest TSP and respirable suspended particulates (RSP) loading among all air monitoring stations in Hong Kong except for the roadside stations. This makes Yuen Long the most polluted area (in terms of TSP and RSP) in Hong Kong, possibly due to the strong sources and the geography of Yuen Long. When a northerly wind prevails in the winter season, Yuen Long is the ideal upwind air monitoring station for Tung Chung.

2.2 Sampling

Samples were collected on quartz-fiber filters using a high-volume sampler (Graseby GMWT 2200) with a Graseby 10 μm inlet (Model 1200). A single impactor stage F (Graseby, Model 231-F) (2.5 μm cut-point) allowed the collection of particles smaller than 2.5 μm. The flow rate was 1.1-1.3 m^3 min^{-1} and the sampling time was nominally 24 h. Samples were stored in 250-ml glass bottles in a refrigerator (~ 0 °C) with 5 ml of methylene chloride added to prevent microbial growth.

2.3 Organic Analysis

The detailed procedures for the analysis of SEOC are presented in Zheng et al. (1997). Briefly, the

filter is ultrasonically extracted with three 200-ml aliquots of dichloromethane, each for 15 minutes at room temperature. The total extract is combined and concentrated to a volume of 3-5 ml by a rotary evaporator (Buchi RE 111). The extract is then filtered and reduced further by gentle evaporation with a stream of high purity N_2 to a volume of 500 µl. The total extract is reacted with 14% BF_3 in methanol to esterify organic acids and then separated into aliphatics, polycyclic aromatic hydrocarbons (PAHs), esters, and alkanols using silica gel packed in a column. Each fraction is subjected to gas chromatography–flame ionization detection (GC-FID, Hewlett Packard Model 5890A gas chromatograph) and gas chromatography–mass-selective detection (GC-MSD, a Hewlett-Packard 5971A mass-selective detector interfaced to a Hewlett Packard Model 5890A gas chromatograph) analyses except for the alkanol fraction, which is converted to trimethylsilyl ethers prior to instrumental analysis. Organic compounds are quantified using the internal standard, hexamethyl benzene. Procedural and solvent blanks are determined and relative response factors are calculated for standard compounds including alkanes, PAHs, methylated fatty acids, phthalates, and alkanols to the internal standard.

3. Results and Discussion

3.1 Comparison of SEOC in $PM_{2.5}$ Collected at HKUST and Tung Chung, July-October

Four sets of samples were collected from HKUST and Tung Chung from July through October 1999. The straight-line distance between the two sites is 36 km. A summary of the total yield, total concentration of each fraction, and important indices such as carbon number preference index (CPI), carbon number maximum (C_{max}), and ratio of the areas of the unresolved to resolved components (peaks) (U:R) is given in Table 1. Definitions of the indices and ratio are in the notes of the table. The daily average wind speed and direction as measured by the Hong Kong Observatory at Waglan Island are also presented. The meteorological data at Waglan Island is commonly considered to represent the background atmospheric conditions at Hong Kong.

The wind for this study period can be divided into three categories. The 6 July samples were collected under a strong southwesterly (SW) wind (6.1 m s^{-1}, 231°); the 7 September samples were collected when a southeast (SE) wind (4.6 m s^{-1}, 122°) was blowing; and an easterly (E) wind (80-84°) prevailed for the remaining two sets of samples (See Table 1).

3.1.1 Total Yield

The total yields, total *n*-alkanes, and total fatty acids are plotted in Figure 2. Figure 3 shows the relationship between total yields and wind directions and speeds.

Table 1. Summary of solvent-extractable organic compounds yields and indices in each fraction.

Sample	SEOC		n-alkanes						n-fatty acids				n-alkanols				PAHs
	Ave. wind	Ave. wind speed, m	Total yield	Total	CPI**	U:R§	UCM	C_{max} @	Total	CPI**	C_{max} @	% plant	Total	CPI* *	% plant	C_{max} @	Total
6-7-99.UST	23	6.1	58.	16.3	1.1	4.5	73	C_{29}	31.0	14.3	C_{16}	19.8	9.1	2.3	63.	C_{28}	1.7
3-8-99.UST	80	4.2	117	15.4	1.3	5.6	86	C_{29}	92.0	8.8	C_{16}	46.5	8.7	6.0	69.	C_{30}	1.5
7-9-99.UST	12	4.6	36.	4.2	1.0	5.7	24	C_{29}	27.3	13.8	C_{16}	7.2	4.1	7.6	54.	C_{28}	0.7
13-10-99.U	84	8.0	71.	19.3	1.2	3.8	74	C_{31}	42.9	6.4	C_{16}	49.7	7.7	6.4	73.	C_{32}	1.2
23-11-99.Y	59	6.3	19	51.1	1.3	3.4	173	C_{29}	123.0	6.3	C_{16}	58.6	12.1	6.2	89.	C_{30}	5.7
14-12-99.Y	17	6.9	74	115.1	1.5	2.1	246	C_{29}	519.6	6.6	C_{16}	57.0	61.6	6.2	87.	C_{30}	49.9
19-1-00.YL	35	8.3	67	168.6	1.3	2.7	457	C_{29}	422.5	10.2	C_{16}	39.9	41.7	5.9	82	C_{30}	43.7
6-7-99.TC			59.	10.9	1.1	5.6	61	C_{29}	38.4	9.4	C_{16}	20.4	9.4	6.6	45.	C_{20}	1.1
3-8-99.TC			19	42.8	1.2	4.3	186	C_{29}	130.9	8.4	C_{16}	46.5	15.3	4.7	69.	C_{30}	3.9
7-9-99.TC			63.	21.4	1.0	6.1	129	C_{26}	34.3	12.7	C_{16}	8.8	5.9	8.7	66.	C_{28}	1.5
13-10-99.T			90.	21.7	1.2	4.7	101	C_{31}	58.7	8.5	C_{16}	35.5	8.6	6.7	84.	C_{28}	1.8
23-11-99.T			16	54.0	1.3	4.1	222	C_{29}	87.3	5.5	C_{16}	62.3	16.6	6.9	91.	C_{30}	2.5
14-12-99.T			71	225.0	1.4	2.9	641	C_{29}	401.6	5.9	C_{16}	62.3	46.9	5.6	88.	C_{30}	40.8
19-1-OO.T			53	173.6	1.3	3.0	519	C_{24}	297.2	7.4	C_{16}	49.3	35.0	5.5	84.	C_{28}	32.2

Note: Concentration in ng m^{-3}. Wind speed and direction are at Waglan Island (Source: Hong Kong Observatory).

*Filtered wind direction and speed. Hourly averaged wind speed less than 2 m s^{-1} is considered to be no wind. The no-wind percentage for the August samples was 43% (1000-1900 hr) and for September it was 21% (0500-0900 hr).

**CPI: Carbon Preference Index, odd-to-even for *n*-alkanes and even-to-odd for *n*-fatty acids and *n*-alkanols.

§ Ratio of branched and cyclic (i.e., hump) to normal hydrocarbons, a measure of the contribution from petroleum residues.

@ C_{max}: carbon number maximum, the carbon number with the highest concentration in that fraction.

The total yield is the sum of the organic compounds extracted from the four fractions. The total yields for the four sets of samples ranged from 36.3 to 192.8 ng m^{-3} and they were higher in Tung Chung than at HKUST (Figure 2). The total yield for this period is usually low because the easterly and southerly winds bring cleaner air from the ocean to Hong Kong (Zheng et al., 2000). The meteorological effect on the total yield will be discussed in a later section on the dispersion of these materials.
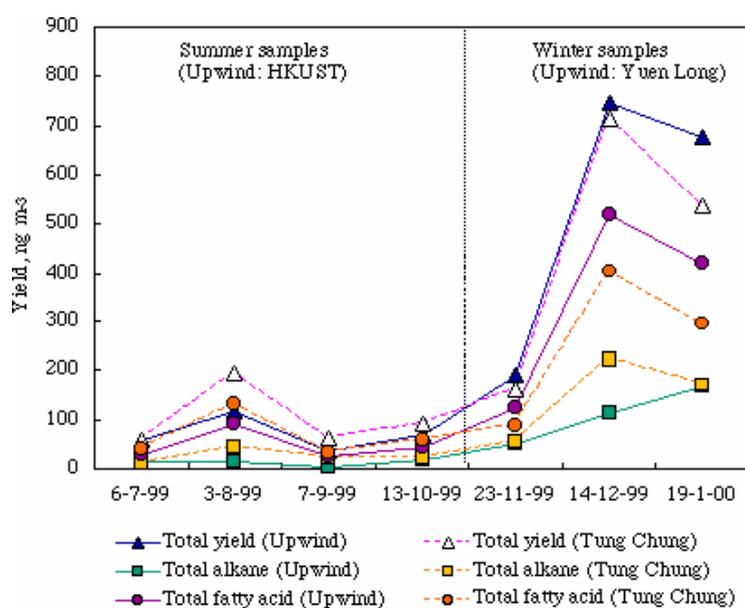
Figure 2. Seasonal variation of total yield, total *n*-alkanes, and total fatty acids.
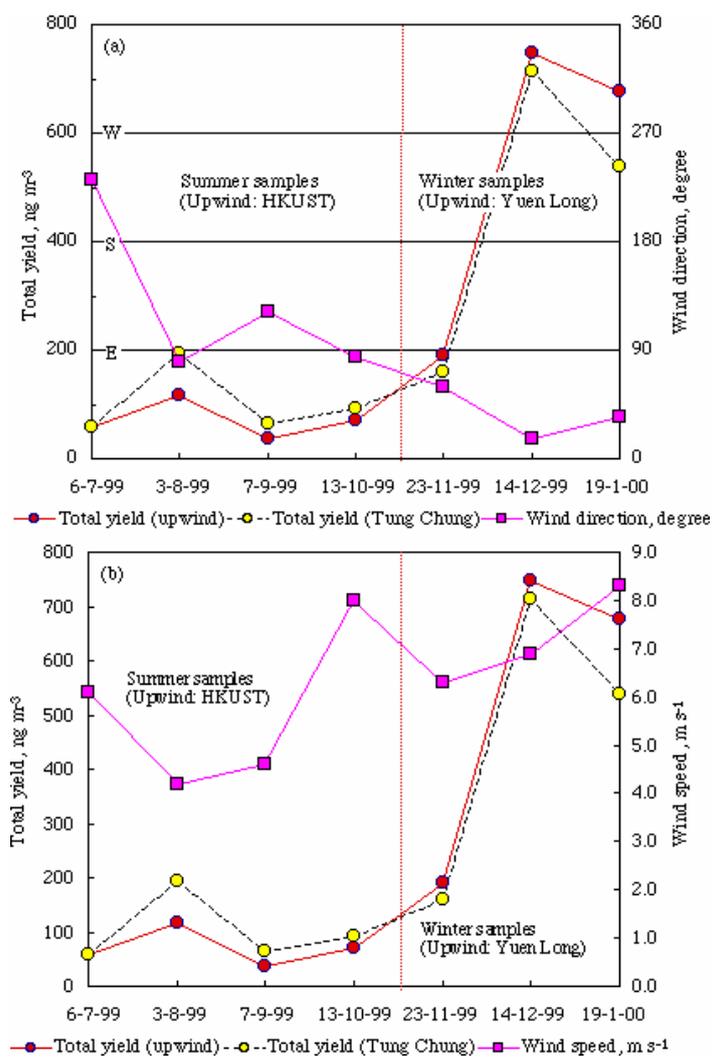

Figure 3. Influence of wind direction (a) and speed (b) on total yield.

3.1.2 *n*-alkanes

Some representative distribution diagrams of the *n*-alkanes, PAHs, fatty acids, and alkanols are shown in Figure 4. The *n*-alkanes (C_{14}-C_{36}) ranged from 4.2 to 42.8 ng m^{-3}, representing 11.5 to 33.8% of the total SEOC. With the exception of the 6 July samples, Tung Chung had a higher alkane concentration than HKUST (Figure 2). The average was 24.2 ng m^{-3} for Tung Chung and 13.8 ng m^{-3} for HKUST, representing 24.2 and 20.0% of the total yield, respectively.

CPI can be used to identify the distribution of recent biogenic matter and anthropogenic materials (Simoneit, 1986). A characteristic of petroleum residues is that CPI equals unity. The CPIs of the *n*-alkanes in our samples were 1.0-1.3, suggesting the presence of vehicular emissions. U:R, also an indicator of contamination by anthropogenic sources (Simoneit, 1986; Zheng et al., 2000), was high and ranged from 3.8 to 6.1. The averaged U:R ratio for Tung Chung was 5.2 and for HKUST it was 4.9. Under the resolved peaks in a typical *n*-alkane gas chromatogram is an envelope of unresolved complex mixture (UCM) that contains branched and cyclic hydrocarbons, which are believed to be contribution from fossil fuel residue (Simoneit, 1986). The trends of UCM for the two sites were similar to the *n*-alkane concentrations with the exception of the 6 July samples. The Tung Chung UCM was significantly higher than at HKUST suggesting the existence of more anthropogenic pollution.

The *n*-alkanes in aerosols can be further divided into two categories: higher plant wax and petroleum residues. The plant wax alkane concentration can be estimated from the following equation (Simoneit et al., 1991):

$$\text{Wax } C_n = C_n - [(C_{n+1}+C_{n-1})/2] \tag{1}$$

where C_n is the concentration of the *n*-alkane with carbon number of n.

The amount of plant wax alkane in the samples was 3.8-14.8%. The average plant wax content for Tung Chung was 8.3% and it was 11.6% for HKUST. This suggests that the bulk of the *n*-alkanes detected at both sites were attributable to petroleum residue sources. The high petroleum residue at Tung Chung may be due to the transport of the city plume (Kowloon Peninsula and Hong Kong) and contribution from the airport. Tung Chung, a new community developed when the airport was built, is not yet urbanized but its aerosols already exhibit city pollution characteristics.

On 6 July, the *n*-alkane concentration at HKUST (16.3 ng m^{-3}) was higher than at Tung Chung (10.9 ng m^{-3}). This could be attributed to the prevailing SW wind which brought clean South China Sea air into the Tung Chung area (Figure 3). Topographically, Tung Chung is exposed from the southwest; therefore, a SW wind can more readily dilute local emissions. On the other hand, HKUST is blocked on the west side by Kowloon Peak, so a SW wind would have less effect on HKUST's environment.
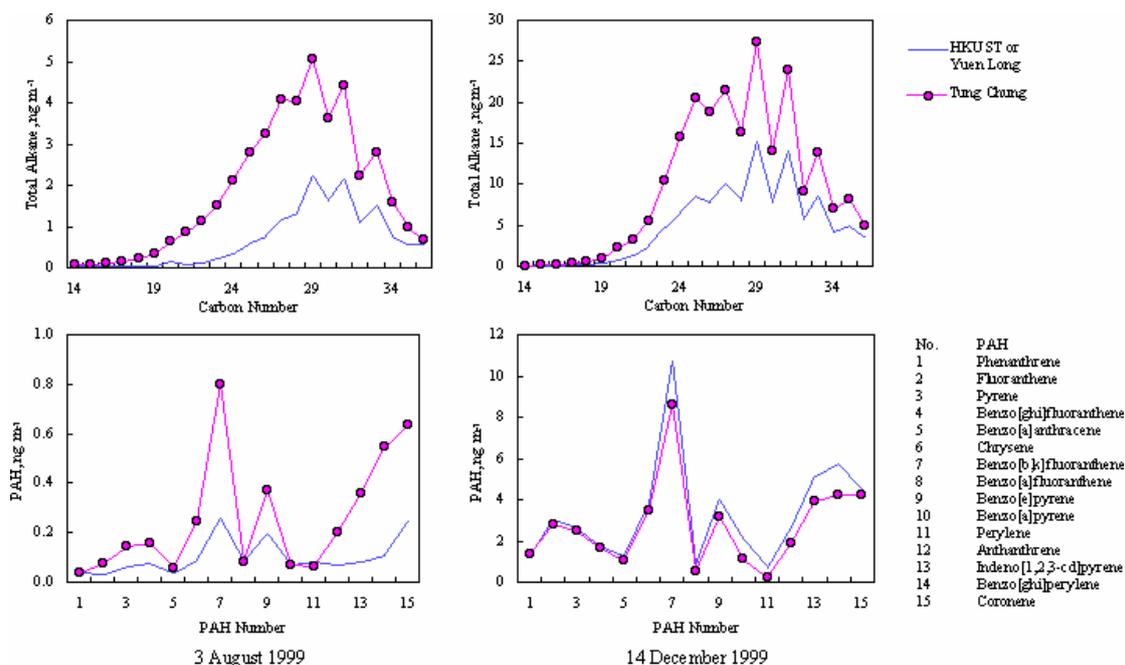
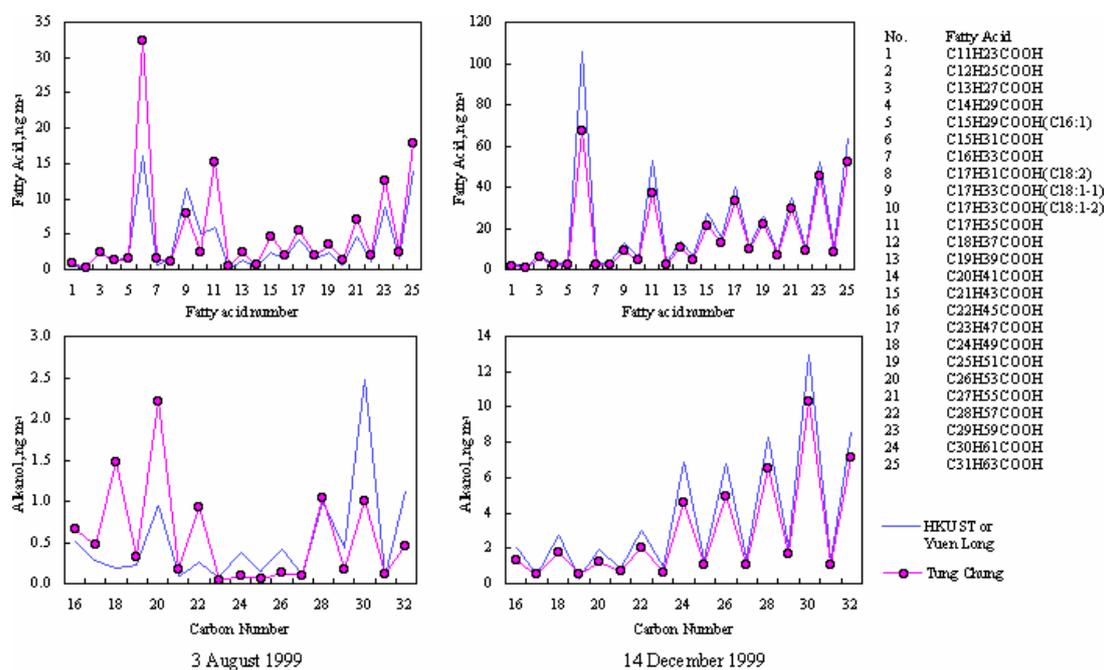**Figure 4.a** Selected distribution diagrams of *n*-alkanes, PAHs, fatty acids, and alkanols.

Figure 4.b Selected distribution diagrams of *n*-alkanes, PAHs, fatty acids, and alkanols

3.1.3 PAHs (Polycyclic Aromatic Hydrocarbons)

Fifteen PAHs were identified (Figure 4). The PAH concentrations were relatively low in this period. The total PAH was 1.1-3.9 ng m^{-3} in the Tung Chung samples and 0.7-1.7 ng m^{-3} in the HKUST samples. The Tung Chung samples showed higher PAH content than those from HKUST except for in July, when southwesterly winds dispersed the pollutants. PAHs represent only a small

fraction (1.3-3.0%) of the total SEOC. The trend of PAH was similar to that of *n*-alkane, suggesting that they were both from the petroleum residue sources of Hong Kong.

3.1.4 Fatty Acids

The concentration range of the fatty acids was 27.2-130.9 ng m^{-3}. The fatty acids constitute 53.4-75.2% of the SEOC, making them the dominant fraction in the samples. Similar to the total yield, Tung Chung had higher fatty acid concentrations than HKUST (Table 1). CPI was calculated based on the C_{12}-C_{32} fatty acids and varied from 6.4 to 14.3. C_{16} was the C_{max} in all samples.

Figure 4 shows the distribution patterns of fatty acids in several representative samples. The $<C_{20}$ homologues are thought to be derived in part from microbial sources while the $>C_{22}$ homologues are from vascular plant wax (Simoneit and Mazurek, 1982). Besides microbial activities, cooking has also been found to be an important contributor of the $<C_{20}$ fatty acids in urban areas (Rogge et al., 1991). Because fatty acids are a large proportion of the SEOC in Hong Kong, the microbial/kitchen fraction of the fatty acids must be regarded as a significant source of atmospheric aerosols. In the Tung Chung samples, the homologues $<C_{20}$ were found to be from 53.8 to 91.2% of all fatty acids and the average was 72.2%. The 3 August and 13 October samples were on the low side, having values of 53.8 and 64.5%, respectively. Likewise, HKUST samples showed low values (53.5 and 50.3%) on these days with a range of 53.5-92.8% and an average of 69.2%. This suggests that the main sources of fatty acids in the summer were emissions from kitchens and microbial activities, followed by vascular plant wax.

The $C_{18:1}/C_{18:0}$ ratio can be used as an indicator of aerosol age because the unsaturated fatty acids are unstable and degrade in the environment due to rapid oxidation (Simoneit and Mazurek, 1982; Kawamura and Gagosian, 1987). In the HKUST samples, this ratio had a range of 0.7-2.7 (average 1.7). $C_{18:1}/C_{18:0}$ was always larger than unity with the exception of the 13 October sample (0.7). In the Tung Chung samples, the values were 0.7-2.8 (average 1.8) and the ratios were always larger than unity with the exception of the 3 August sample at 0.7. The high $C_{18:1}/C_{18:0}$ ratios in the summer samples, especially for July through September, can be taken as an indication that the fatty acids have a local origin.

3.1.5 Alkanols

The detectable alkanols ranged from C_{16} to C_{32} with even-to-odd predominance (Figure 4) (CPI in the range of 2.3-8.6). The Tung Chung CPI was always higher than that of HKUST with the exception of 3 August. The total alkanol concentration range was 4.1-15.3 ng m^{-3} and Tung Chung was higher than HKUST. The homologues $>C_{20}$ are characteristic of vascular plant wax and the homologues $<C_{20}$ could be derived from microbial sources (Simoneit, 1986; Eglinton and Hamilton, 1963). The microbial source contribution was in the range of 26.5-54.6% for HKUST and the average was 34.7%,

while for Tung Chung it was 15.8-54.6% and the average was 33.6%. These samples show that plant wax was the main contributor of alkanols with microbial activities playing a secondary role.

3.2 Dispersion of $PM_{2.5}$, July-October

The 6 July HKUST samples showed higher *n*-alkane and PAH concentrations than the Tung Chung samples, while the reverse was true for the rest of the samples. The main reason was the relatively strong prevailing southwesterly wind at 6.1 m s^{-1} on 6 July which cleaned up Tung Chung's atmosphere (Figure 3). The sources of SEOC were mainly local and fresh.

The highest total yields were recorded on 3 August at 192.8 and 117.6 ng m^{-3} in the Tung Chung and HKUST samples, respectively. The PAH concentration in the Tung Chung samples increased accordingly to 3.9 ng m^{-3}, yet it represented only 2.0% of the total SEOC; the PAH concentration in the HKUST sample was only 1.5 ng m^{-3} and 1.3% of the total SEOC. From Figure 3, we can see that the relatively low wind speed (4.2 m s^{-1}) and long periods of no wind (43% of the sampling time) were responsible for this phenomenon, even though the prevailing wind was easterly. In the calculation of wind directions and speeds, any hourly average wind speed less than 2 m s^{-1} was designated as "no wind" because automatic weather stations may not be able to measure wind directions accurately at lower speeds. The long no-wind period (1000 to 1900 hr, straddling the morning and evening traffic rush hours) at the beginning of the sampling period and the 10-hour no-wind period prior to sampling suggest there was an accumulation of pollutants emitted the previous day. Once the wind started to pick up, the wind speed was still relatively low and did not help disperse air pollutants, resulting in high concentrations at both sites. Being downwind, Tung Chung may also be affected by the city plume. Because of accumulation (longer residence-time), the unsaturated $<C_{20}$ homologues of the fatty acids had more time to oxidize, thus, lowering the $C_{18:1}/C_{18:0}$ fatty acid ratio. This is an indication of the presence of aged aerosols.

For the 7 September samples, the total yields were low: 63.1 ng m^{-3} at Tung Chung and 36.3 ng m^{-3} at HKUST. Likewise, the PAH concentration at Tung Chung (1.5 ng m^{-3}) was two times higher than HKUST (0.7 ng m^{-3}). The prevailing wind was east-southeast at an average speed of 4.6 m s^{-3}. The no-wind period was 21% (0500 to 0900 hr). Compared to the conditions of the August samples, much cleaner air from the South China Sea was sweeping across Hong Kong. Evidence of local sources can be established from *n*-alkane CPI (1.0 for both locations), high U:R ratios (5.7 at HKUST and 6.1 at Tung Chung), high microbial contributions (92.8% at HKUST and 91.2% at Tung Chung), and $C_{18:1}/C_{18:0}$ ratios (2.8 at HKUST and 2.1 at Tung Chung).

The two 13 October samples taken at HKUST and Tung Chung are very close in total yield concentrations and a shift of C_{max} to a higher carbon number (C_{29} to C_{31}) is evident in both samples. The wind direction was 84 ° and wind speed was high at 8.0 m s^{-1}. The plant wax contribution in the *n*-alkanes was higher at 14.8% for HKUST and 13.0% for Tung Chung. There was also a significant increase in the plant wax contribution in the fatty acids (49.7% for HKUST and 35.5% for Tung

Chung) (see Figure 5) and the $C_{18:1}/C_{18:0}$ ratios decreased. Tung Chung is in the path of the city plume under prevailing easterly wind conditions; thus, the petroleum residue portion of the SEOC should be higher than at HKUST.
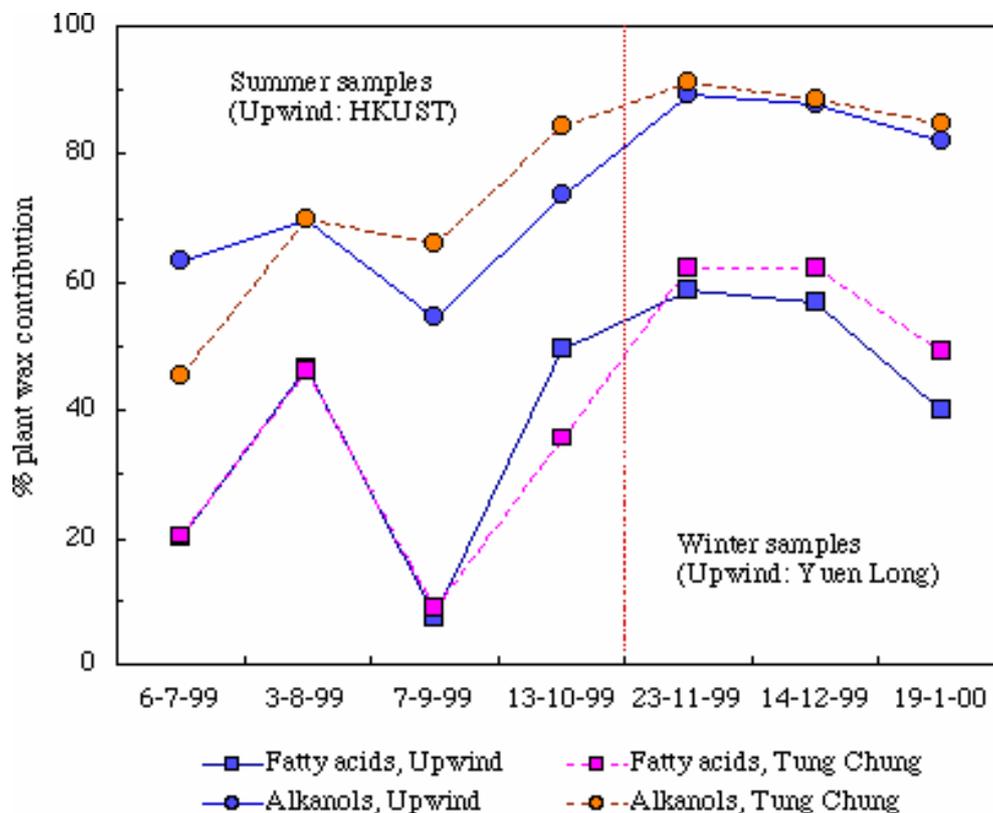

Figure 5. Plant wax contribution in fatty acids and *n*-alkanols.

3.3 Comparison of SEOC in PM$_{2.5}$ Collected at Yuen Long and Tung Chung, November- January

The straight-line distance between the two sampling sites, Yuen Long and Tung Chung, is 22 km. The wind direction during this period can be divided into two categories: east-northeast (ENE) (59°) on 23 November and northeast (NE) on 14 December 1999 (17°) and 19 January 2000 (35°). The winds were strong, ranging from 6.3 to 8.3 m s^{-1}.

3.3.1 Total yields

The total yields of the three sets of samples were 160.4-746.2 ng m^{-3} and within each set of samples the yields were similar (Table 1). The Yuen Long samples displayed a higher total yield concentration than those from Tung Chung. The total yield in the Tung Chung samples was significantly higher in the winter than in the summer.

3.3.2 *n*-alkanes

The *n*-alkane concentration at Yuen Long was 51.1-168.6 ng m^{-3} representing 15.42-26.6% of the total SEOC, while at Tung Chung it was 54.0-225.0 ng m^{-3} and 31.5-33.6%. Tung Chung had a higher *n*-alkane concentration than Yuen Long, but the opposite was true for total yield, *n*-alkanoic acids and PAHs. The winter Tung Chung *n*-alkane concentrations were higher than the values in the warmer months reported earlier.

The winter CPI of the alkanes was 1.3-1.5 and was higher than that of the summer. Tung Chung had lower winter CPI than Yuen Long did. The U:R ratio was 2.7-4.1, with Yuen Long lower than Tung Chung. This suggests that the *n*-alkanes in the Tung Chung samples were more mature than those in the Yuen Long samples, and the Tung Chung samples exhibited more distinct anthropogenic characteristics. The trend of UCM was similar to the alkanes, with the Tung Chung UCM (222-641 ng m^{-3}) always being higher than the Yuen Long UCM (173-457 ng m^{-3}). This suggests that Tung Chung in these months experienced poorer air quality than Yuen Long in terms of alkanes, and Yuen Long has been demonstrated to be one of the most polluted areas in Hong Kong (Air Quality in Hong Kong 1998). C_{max} of alkane is C_{24} and C_{29}.

The plant wax in the *n*-alkanes of the winter samples was 13.2-17.7% for Tung Chung and 14.8-20.2% for Yuen Long. This suggests that over 80% of the *n*-alkanes obtained from both sites were of anthropogenic origin with Tung Chung having the higher share.

3.3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

There was a larger spread in PAH concentration in the winter samples ranging from 2.5 to 49.9 ng m^{-3}; the average for Yuen Long was 33.1 ng m^{-3} (5.4% of total yield) and for Tung Chung   it was 25.1 ng m^{-3} (4.4% of total yield). The PAH concentration and its relative amount in SEOC in the Yuen Long samples were higher than those in the Tung Chung samples. This is contrary to the *n*-alkanes, suggesting that they may not be of the same origin. The additional PAHs could come from non-vehicular combustion sources such as coal and biomass burning.

The higher winter PAH concentration followed the same trend as total yield, *n*-alkanes, *n*-alkanoic acids, and *n*-alkanols. The 14 December and 19 January Tung Chung samples had PAH values of 40.8 and 32.2 ng m^{-3}, respectively. The lone high PAH summer sample at Tung Chung was on 3 August at 3.9 ng m^{-3}, which was lower than the 14 December sample and 8.3 times lower than the 19 January sample. The same was true for Yuen Long. The Tung Chung samples for November had low a PAH concentration (2.5 ng m^{-3}) and proportion (1.6% of total yield). This suggests that the 14 December and 19 January samples were different from the rest of the samples in that other sources may be present in addition to local sources. The wind direction was 17° on 14 December and 35° on 19 January, making the transport of airborne material from Shenzhen possible.

Another possible explanation for the high PAH concentrations in winter is that they are

semi-volatile and can exist in both gas and particulate phases in the atmosphere (Bidleman et al., 1986). For the same emission rate, more PAHs are expected in the vapor phase in the summer due to the higher temperature; however, in winter, they tend to be in the particulate phase (Zheng and Fang 2000; Zheng et al., 2000).

3.3.4 Fatty Acids

The concentration of fatty acids was 87.3-519.6 ng m^{-3} and constituted for more than half of the SEOC at 54.5-69.4%. Yuen Long had higher fatty acid concentrations than Tung Chung did, which was similar to the case with total yield (Table 1). The CPI varied from 6.4 to 14.3. The average CPI for Tung Chung was 9.8 and for Yuen Long it was 10.8. C_{16} was the C_{max} in all samples.

In the Tung Chung samples, the $>C_{22}$ homologues were found to be higher than the $<C_{20}$ homologues, except for the 19 January samples, when the reverse was true. This means the relative concentrations of the plant wax in the fatty acids were higher in winter than in summer. One possible reason is the strong wind abrasion of leaves in the winter (Zheng et al., 2000). The other possible source of plant wax is the Maipo Wetland. If long-distance transport were a factor, even more vascular plant wax contribution would be observed in the samples (Fang et al., 1999).

The $C_{18:1}/C_{18:0}$ ratio at Yuen Long was less than unity, suggesting that the fatty acids were aged. This lower ratio could be due to the influx of outside (possibly Shenzhen) aged aerosols transported by the winter winds. In general, the fatty acids in the Tung Chung samples exhibited the same behavior with the exception of the 23 November sample, in which the plant wax contribution was higher than the kitchen and microbial emissions. However, the $C_{18:1}/C_{18:0}$ ratio was 1.2, which suggests that the fatty acids had local contributions and may also be influenced by the city plume.

In the 23 November samples,the total yields and PAHs were relatively low and resembled summer aerosols in terms of loading. But the plant wax fraction in the fatty acids showed a marked increase, resembling winter aerosols (Figure 5). This change in the plant wax contribution in fatty acids could be an indicator of a change in climate or season.

3.3.5 Alkanols

The alkanols in the Tung Chung and Yuen Long samples were 12.1-61.6 ng m^{-3}. CPI was 5.5-6.2 and the C_{max} was C_{30} with the exception of the 19 January sample, when it was C_{28}. The average higher plant wax in the *n*-alkanols was 88.1% of all alkanols in the Tung Chung sample and 86.3% for Yuen Long. When compared to the summer value of 66.4% in Tung Chung, this suggests that the main source of the alkanols in winter was vegetation. By the same token, as argued for the fatty acids, the plant wax contribution in alkanols could also be used as an indicator of the change of season (Figure 5).

3.4 Dispersion of PM$_{2.5}$, November-January

Out of the three samples studied, the loading of the 23 November sample was more like that of the summer samples mainly because of the prevailing wind (59°). This suggests that the influence of Shenzhen on Yuen Long and on the more distant Tung Chung was not pronounced. There were, however, dramatic increases in all the yields in the 14 December and 19 January samples when the wind was northerly.

The 14 December samples had the highest yields. The wind direction was 17°. The total yields in the Tung Chung and Yuen Long samples were 714.3 and 746.2 ng m^{-3}, respectively, and the total PAHs were 40.8 and 49.9 ng m^{-3}. Higher alkane CPI, more plant wax in the SEOC, and lower U:R and C$_{18:1}$/C$_{18:0}$ ratios were observed. All these suggest the possible intrusion of outside aerosols. Under this meteorological condition, Yuen Long (being closer to Shenzhen) is expected to be more influenced by the sources in Shenzhen. Furthermore, because of the topography, a north wind is more likely to trigger the accumulation of air pollutants in Yuen Long. On the other hand, the city plume probably would have little impact on Yuen Long. The presence of the Maipo Wetland could also have an impact on Yuen Long's air quality. Tung Chung experienced a similar situation, with the exception of a much higher *n*-alkane yield and UCM. Local emissions and non-local plumes may be the cause.

Much the same can be said about the January samples, with slight differences. Compared with the 14 December sample from Tung Chung, the *n*-alkanes had lower CPI and wax content, higher U:R, less plant wax contribution in the fatty acids, and higher C$_{18:1}$/C$_{18:0}$ ratios. These data suggest that the January samples had more urban characteristics, although the influence from outside was also distinct.

4. Conclusions

Seven sets of PM$_{2.5}$ samples were collected from Tung Chung, Yuen Long, and HKUST from July 1999 to January 2000, straddling the summer and winter seasons in Hong Kong. The organic compounds extracted included *n*-alkanes, fatty acids, *n*-alkanols, and PAHs, and they originated from petroleum residue, kitchen exhaust, microbial activities, and vascular plant wax. The sources are local but there is evidence of an influx when the wind is from the north. Plant wax contributions in the fatty acids and *n*-alkanols may be used as an indicator of the change in season.

Five different wind directions were detected: SW and SE (oceanic), E (oceanic wind over the main pollution sources in Kowloon Peninsula and North Hong Kong), ENE (transition between oceanic and continental) and NE (continental). The winds dilute local emissions with cleaner oceanic air, transport the city plume to the downwind site, and import air masses with aged aerosols from the surrounding regions to form a mixture with freshly generated local particulates. When the wind speed is low, accumulation takes place, resulting in high aerosol loading in the atmosphere.

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