Seasonal variations and mass closure analysis of particulate matter in Hong Kong

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Abstract

The chemical characteristics of ambient particulate matters in urban and rural areas of Hong Kong were determined in this study. A monitoring program starting from November 2000 to February 2001 (winter) and June 2001 to August 2001 (summer) for PM\textsubscript{10} and PM\textsubscript{2.5} was performed at three monitoring stations in Hong Kong. Twenty-four-hour PM\textsubscript{10} and PM\textsubscript{2.5} samples were collected once every 6 days at two urban sites, PolyU and KT, and every 12 days at a background site, HT, with Hi-Vol samplers. High concentrations of OC, EC (except in PolyU), water-soluble ions and elements were observed in winter among the three sampling sites for PM\textsubscript{10} and PM\textsubscript{2.5} fractions. Seasonal variations were significant in background HT. Dilution effect due to the increase in mixing depth and precipitation in summer reduced the concentrations of particulate matters. Long-range transport could contribute to the higher concentrations of particulate matter in the winter.

Chemical mass closure calculations were performed for PM\textsubscript{10} and PM\textsubscript{2.5} observed. Mass closure improved when separate factors (1.4 and 1.9 respectively) were used to convert water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WINSOC) into corresponding organic masses. The urban sites showed high percentages of water-soluble ions in winter and high percentages of carbonaceous species in summer. Seasonal variations were significant in background HT. Dilution effect due to the increase in mixing depth and precipitation in summer reduced the concentrations of particulate matters. Long-range transport could contribute to the higher concentrations of particulate matter in the winter.

1. Introduction

Particulate matters (PM) in the atmosphere originate from either direct emission or physical and chemical
transformation of gaseous pollutants. The major sources of atmospheric particulates are fossil-fuel combustion (which produces fly ash and soot), industrial processes (involving metals, fibers, etc.), transportation, wind and soil erosion (producing fugitive dust), and photochemical reactions (complex chain reactions between sunlight and gaseous pollutants). Because of the large number of sources, PM may contain hundreds of different chemical species. The PM$_{10}$ is generally measured only when new particles have been recently formed or when fresh emission sources are close to a measurement site (Lundgren and Burton, 1995). Some of the PM$_{2.5}$ is formed by nucleation, condensation and gas-phase reactions of smaller particles (Hoppel et al., 1990; Lin, 2002). Therefore, efforts have been made over the years to elucidate the chemical composition of atmospheric aerosols as a function of size, and to achieve mass closure on the chemical species for the whole mass of aerosol collected (Matta et al., 2003).

Hong Kong is located on the coast of western Pacific Ocean (114° 15’ E, 22° 13’ N). On the north and west is the Asian continent, and to the south and east is the Pacific Ocean. It is on the boundary region of land and sea, thus it experiences different weather induced by the different heating capacity of the two media. The weather changes lead to sharp changes of aerosol levels and composition across seasons. To the north of Hong Kong, the Asian continent is a well-known pollution source (Louie et al., 2005). In contrast, there is little emission in the sector of southeast to southwest for a few hundred kilometers. Hong Kong is one of the most densely populated places in the world. Air quality has become an issue of major concern. Previous works in determining PM in Hong Kong tended to concentrate on the TSP and PM$_{10}$ size fractions (Panther et al., 1999; Fung and Wong, 1995). However, there have been limited studies on PM$_{2.5}$ with respect to their chemical composition (Cheng et al., 2000) and seasonal variations. Full chemical characterization of PM$_{2.5}$ is essential to the development of control strategies. The monitoring results by the Hong Kong Environmental Protection Department (HKEPD) indicate that diesel vehicular exhaust is the major cause of high PM$_{10}$ level in urban roadside area in Hong Kong (Chan and Kwok, 2001). The chemical characteristics of atmospheric aerosols have been studied in the urban and rural area (Fung and Wong, 1995; Qin et al., 1997; Lam et al., 1997; Cheng et al., 2000). Next to particulate carbon, SO$_4^{2-}$, NH$_4^+$ and NO$_3^-$ were the second most important groups of chemical components of PM$_{10}$. The objective of this study is to determine the spatial variations of the chemical compositions (OC, EC, water-soluble ions and elements) of PM$_{10}$ and PM$_{2.5}$ at the three monitoring stations during winter and summer. Mass closure of PM$_{2.5}$ and PM$_{10}$ were used to differentiate the relative contributions of these chemical species.

2. Methodology

2.1. Sampling sites

Three locations, Hung Hom (where the Polytechnic University campus, or PolyU, is located), Kwun Tong (KT), and Hok Tsui (HT) were selected for PM monitoring. They are shown in Fig. 1, and the site descriptions are given as follows:

Hung Hom (PolyU): It is approximately 6 m above ground, and 8 m away from a main traffic road. The station is adjacent to Hong Chong Road, which leads to the Cross Harbor Tunnel. The traffic volume of the road is extremely high, in excess of 170,000 vehicles per day. The site faces the Victoria Harbor, with a strong sea breeze providing good air dispersion. Thus the particulate levels at this site are mainly influenced by vehicular emission.

Kwun Tong (KT): This site was selected for data comparability as it is also one of the HKEPD’s air quality monitoring stations. It is close to residential buildings, and most of the vehicles are light and heavy trucks. The area represents a mixed residential/commercial/industrial area. The samples were collected on the rooftop, approximately 25 m above ground.

Hok Tsui or Cape D’ Aguilar (HT): HT is located near the sea at the southeastern tip of the Hong Kong Island. Since the prevailing winds for Hong Kong are southerly in summer and easterly in the other seasons, this site is seldom downwind of the urban plume of Hong Kong and is considered as
one of the best locations for regional studies in the southern China region.

2.2. Sampling methods

A particulate monitoring program from November 2000 to February 2001 and June 2001 to August 2001 was conducted at the three monitoring stations, collecting 24 h PM$_{10}$ and PM$_{2.5}$ samples once every 6 days at the PolyU and KT stations, and every 12 days at HT. Two high volume (hi-vol.) samplers (Andersen Instruments/GMW) operated at 1.13–1.41 m$^3$ min$^{-1}$ were used to collect PM$_{10}$ and PM$_{2.5}$ samples on 20.3 × 25.4 cm prefired (900 °C for 3 h) Whatman quartz microfiber filters (to reduce the blank level of carbonaceous in the filters). The filters were weighed using a balance (Sartorius, Analytic) with an accuracy of 0.1 mg after conditioning in an electronic desiccator (RH=40% and temperature=25 °C) before and after sample collection for 24 h. After weighing, loaded filters were stored in a refrigerator at about 4 °C before chemical analysis to prevent the evaporation of volatile components. Also, field blank filters were collected to subtract the positive artifacts due to adsorption of gas-phase components onto the filter during and/or after sampling. The hi-vol filters permitted filter sections with sufficient mass loading for the various chemical analyses.

2.3. Particulate matters analysis

After sampling, the filters were conditioned and reweighed to determine the particulate mass. The filters were then sectioned for individual analyses. The filters were analyzed with thermal/optical reflectance (TOR) method for organic carbon (OC) and elemental carbon (EC), ion chromatography (IC) for ions, atomic absorption spectrophotometry (AAS) for sodium and potassium, and inductively coupled plasma-mass spectrometry (ICP-MS) for elements. The chemical analyses were carried out by the Air Laboratory of PolyU (OC, EC, and elements), Hong Kong University of Science and Technology (water-soluble ions), Zhongshan University (microwave digestions of filters for element analysis) and The Chinese University of Hong Kong (heavy metals).
2.4. Carbonaceous species analysis

The samples were analyzed by the selective thermal manganese dioxide oxidation (TMO) with a modified Dohrmann DC-52 carbon analyzer at AtmAA Inc., Calabasas, CA, USA (Fung, 1990) and a DRI Model 2001 Thermal/Optical Carbon Analyzer in the Air Lab of The Hong Kong Polytechnic University, Hong Kong According to the IMPROVE (TOR) protocol (Chow et al., 1993; Cao et al., 2003). Previous comparison results between TMO and TOR showed good agreement in TC, OC and EC (Fung et al., 2002). Inter-laboratory comparison between PolyU’s instrument and TMO (AtmAA, Inc) also showed good agreement. The difference determined from replicate analyses was smaller than 5% for TC (total carbon), and 10% for OC and EC.

2.5. Water-soluble ions analysis

Quarter sections of the filters were extracted by using 10 ml of ultra-pure water (specific resistance ≥18.1 MΩ cm). The extraction solutions were filtered and stored in plastic vials in the refrigerator at 4℃ until chemical analysis. Water-soluble ions were measured using ion chromatography (DIONEX 500) with an electrochemical detection (DIONEX ED40) by the Department of Chemical Engineering of Hong Kong University of Science and Technology (HKUST). Uncertainties were ±6% for Cl⁻ and were ±12% for NO₃⁻, SO₄²⁻ and NH₄⁺.

2.6. Element analysis

Strips of 1/8 of the sample filters were digested using a laboratory microwave digestion system to extract metals with a hydrochloric/nitric acid solution (USEPA Methods IO 3.1, 1999) in the Department of Chemistry, Zhongshan University. The digestate was filtered and then diluted to 25 ml with distilled–deionized water. The solution was then analyzed by different instruments. Sodium and potassium (Na and K) were determined by AAS (Perkin-Elmer 3300 Atomic Absorption Spectrophotometer). Major crustal elements (Al, Ca, Fe and Mg etc.) were analyzed by ICP-AES (Perkin-Elmer, OPTIMA 3300DV) and trace metals (As, Cr and Cu etc.) were analyzed by ICP-MS (HP 4500). The ICP-AES and ICP-MS were calibrated using a high-purity standard solution. The sample solutions were measured in triplicates, and quality controls and blanks were inserted at every 20 samples. The relative standard deviations of the measured element concentrations were typically <5%. Precision and bias were <10%. Element concentrations of the procedural blanks were generally <5% of the samples.

3. Results and discussion

3.1. PM₁₀ and PM₂.₅

A total of 140 samples of PM₁₀ and PM₂.₅ were collected in this study. Statistics for particulate concentrations at the different sites in the winter and their PM₁₀ and PM₂.₅ ratio are shown in Table 1. The average concentrations at these three sites ranged from 47.65 to 73.53 µg/m³ for PM₁₀, and from 28.20 to 42.59 µg/m³ for PM₂.₅. Among the 3 sites, the average concentration of PM₁₀ at PolyU was the highest (73.53 µg/m³), reflecting the high emission sources (e.g. vehicular emission exhaust) around this station. The highest daily mass concentrations of PM₁₀ and PM₂.₅ were observed at KT in winter (125.89 µg/m³ and 116.89 µg/m³ respectively), and the average PM₂.₅ concentrations level measured in KT (42.59 µg/m³) is higher than HT (28.20 µg/m³) and is similar to PolyU stations (41.24 µg/m³). The reason for this observation could be the high traffic flows at KT, coupled with the emissions from the nearby industrial areas and restaurants. The average concentration of PM₂.₅ observed at HT (28.20 µg/m³) were lower than the others, due its distance from the urban district of Hong Kong and the high dispersion from sea wind.

<table>
<thead>
<tr>
<th>Concentrations</th>
<th>Location</th>
<th>Max.</th>
<th>Min.</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM₁₀ (µg/m³)</td>
<td>PolyU (n=28)</td>
<td>114.62</td>
<td>39.81</td>
<td>73.53</td>
<td>20.94</td>
</tr>
<tr>
<td></td>
<td>KT (n=28)</td>
<td>125.89</td>
<td>29.02</td>
<td>55.75</td>
<td>23.84</td>
</tr>
<tr>
<td></td>
<td>HT (n=14)</td>
<td>122.01</td>
<td>12.19</td>
<td>47.65</td>
<td>19.29</td>
</tr>
<tr>
<td>PM₂.₅ (µg/m³)</td>
<td>PolyU (n=28)</td>
<td>63.56</td>
<td>19.43</td>
<td>41.24</td>
<td>12.37</td>
</tr>
<tr>
<td></td>
<td>KT (n=28)</td>
<td>116.89</td>
<td>20.12</td>
<td>42.59</td>
<td>21.03</td>
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<tr>
<td></td>
<td>HT (n=14)</td>
<td>58.20</td>
<td>5.12</td>
<td>28.20</td>
<td>19.29</td>
</tr>
</tbody>
</table>
However, the concentration levels of PM$_{10}$ at HT station is only slightly less than the KT station. The source of the particulate matter in this case is most likely marine aerosol (see the Water-soluble ions section).

3.2. OC and EC

Generally speaking, higher concentrations of OC were observed in winter than in summer at all the sampling sites. The average OC concentrations in both PM$_{10}$ and PM$_{2.5}$ fractions at the urban sites (PolyU and KT) ranged from 9.45 to 12.02 $\mu$g/m$^3$ during winter periods and from 5.61 to 9.48 $\mu$g/m$^3$ during the summer. The difference at background HT site was significant (Table 2, Fig. 2). In general, the following factors could affect the concentrations of OC during both the winter and summer: dilution, due to the increased mixing depth found in summer (Sequeira and Lai, 1998); more rainy days in the summer, causing the particulate matters to be washed out in the atmosphere; and physical dispersion/transport which could be the reasons for higher concentrations of OC and EC in winter. The prevailing winds in Hong Kong are northeasterly, especially during wintertime. Thus the transportation of pollutants from the Asian Continent could be contributing to the levels observed at the background site.

However, there was no significant difference for the concentrations of EC at PolyU station. The distance between the source (on-road vehicles) and the sampling location (PolyU station) was short ($<20$ m). As the dominant source for EC was vehicular emission, no variations of EC (PM$_{10}$: winter EC=6.86 $\mu$g/m$^3$, summer EC=6.89 $\mu$g/m$^3$) were observed at PolyU station. But when the sampling location was set-up at a rooftop as in KT and at the background HT site, low EC concentrations were observed in the summer (HT EC concentrations: 0.42 $\mu$g/m$^3$ for both fractions).

PM$_{2.5}$ at PolyU station consists of 18.18% OC and 11.16% EC (total carbon, TC=OC+EC near to 30%, Fig. 3) in the winter, while in the summer it consists of

<table>
<thead>
<tr>
<th>Sample category</th>
<th>Sampling site</th>
<th>OC concentration (winter)</th>
<th>EC concentration (winter)</th>
<th>OC concentration (summer)</th>
<th>EC concentration (summer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>PolyU</td>
<td>9.45 ± 2.01</td>
<td>5.80 ± 1.14</td>
<td>7.96 ± 2.77</td>
<td>6.12 ± 0.74</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>PolyU</td>
<td>12.02 ± 2.00</td>
<td>6.86 ± 1.16</td>
<td>9.48 ± 2.99</td>
<td>6.89 ± 2.52</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>KT</td>
<td>10.16 ± 2.59</td>
<td>5.05 ± 1.01</td>
<td>5.61 ± 2.23</td>
<td>4.33 ± 0.57</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>KT</td>
<td>10.36 ± 2.58</td>
<td>5.09 ± 0.95</td>
<td>6.47 ± 2.51</td>
<td>4.33 ± 0.54</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>HT</td>
<td>5.52 ± 1.13</td>
<td>1.36 ± 0.40</td>
<td>1.49 ± 0.27</td>
<td>0.42 ± 0.07</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>HT</td>
<td>5.62 ± 1.08</td>
<td>1.48 ± 0.36</td>
<td>1.68 ± 0.38</td>
<td>0.42 ± 0.07</td>
</tr>
</tbody>
</table>

Fig. 2. The variations of OC and EC in PM$_{2.5}$ during winter and summer among three monitoring sites.
24.34% OC and 18.71% EC (TC = 43%). The percentages of TC in PM$_{10}$ and PM$_{2.5}$ were higher at the urban sites (PolyU and KT) than at the nonurban sites (HT). Also the mass percentage of OC and EC in both PM$_{10}$ and PM$_{2.5}$ fractions were higher in summer than in winter at the three monitoring sites.

### 3.3. Water-soluble ions

The winter/summer variations of water-soluble ions were shown in Figs. 4 and 5. Higher concentrations of ions were observed in the winter among all the sampling sites for both fractions. The large contrast between winter and summer is attributed to the Asian monsoon system described in the previous section. Both clean marine air masses and wash out effects caused by high precipitation contribute to the low concentration seen in the summer. On the other hand continental outflow which passes through vast source areas and the dry and cold conditions that prolongs the life of many pollutants contributed to high aerosol mass concentrations of water-soluble ion in the winter (Lam et al., 1997).
On average, $\text{SO}_4^{2-}$ concentration in the winter was 3.3 to 7.7 times higher than in the summer. This extremely large difference implies a significant $\text{SO}_4^{2-}$ source in the winter. $\text{SO}_4^{2-}$ concentration at PolyU and KT were similar for both winter and summer for PM$_{10}$ and PM$_{2.5}$, suggesting regional source may also be contributing. The concentrations of $\text{SO}_4^{2-}$ at HT were slightly lower than urban areas. Thus the source of $\text{SO}_4^{2-}$ could be mainland China, carried by long-range transportation. In the summer the concentrations of $\text{SO}_4^{2-}$ for PM$_{10}$ and PM$_{2.5}$ were 2.80 and 1.69 $\mu$g/m$^3$ respectively at the HT site.

Similar situation was observed for nitrate. The concentrations of NO$_3^-$ in the winter was about 4 times higher at urban areas and 15 times higher at HT than in the summer for PM$_{10}$. At the same time the concentrations of NO$_3^-$ in the winter was about 7–8 times higher at urban areas and 93 times higher at HT than in the summer for PM$_{2.5}$. Low concentrations of NO$_3^-$ were observed at HT for PM$_{10}$ (0.29 $\mu$g/m$^3$) and PM$_{2.5}$ (0.01 $\mu$g/m$^3$) in the summer. However, the difference of nitrate concentrations between urban area and rural area were not significant in the winter. The partition of NO$_3^-$ between the gas and particulate phases depends strongly on temperature ($T$), relative humidity (RH) and ammonia concentration. Although there are no dramatic variations of RH in Hong Kong, the temperature does rise above 30 °C in the summer, which causes large variations of NO$_3^-$. And the PM$_{2.5}$ to PM$_{10}$ ratios of nitrate changed from 0.43 and 0.30 to 0.21 and 0.05 at PolyU and HT respectively. This shows there are more nitrate distributed in coarse mode in the summer, as fine mode nitrate (mainly ammonium nitrate) are unstable at high temperature and tend to dissociate into gases nitric acid and ammonium.

Higher concentrations of particulate NH$_4^+$ were observed in winter than in summer at the three monitoring sites. This can be attributed to the equilibrium of thermal decomposition of ammonium chloride and ammonium nitrate in the winter, and to the long-range transport of pollutants in the winter. The higher ammonium concentrations in PM$_{2.5}$ during the summer may be due to sampling artifacts and evaporation of volatile ammonium ion to the gas phase in the higher temperature. However, since SO$_2$, NO$_x$ and NH$_3$ were not measured in our monitoring program, we do not know whether SO$_2$, NO$_x$ and NH$_3$ supplies were also higher in the winter.

It has been demonstrated that all three sites had the highest concentrations of Na$^+$ and Cl$^-$ in the winter. The concentrations of Na$^+$ in the winter were about 2 times higher in the summer for both fractions at PolyU and KT (urban sites). However, this difference was
also significance at the background HT site. HT had the highest average concentrations of Na\(^+\) in the winter and in the summer for PM\(_{10}\). One of the ways sea salt particles can be produced is by the bursting of sea water bubbles on the surface of sea, and this process is nearly linearly dependent on wind speed, especially when the wind speed in the marine boundary layer is relatively high (Despiau et al., 1996). Consequently it appears that in winter the largest amount of sea salts were blown from the ocean to the HT station with the least amount of sea salts being washed out by rainfall.

3.4. Elements

In Table 3, the average values of the elemental concentrations are listed for winter and summer period. The absolute concentration of the various metals is highly differentiated. Generally speaking, high concentrations of crustal elements, such as Al, Ca and Fe were observed among the three stations especially in PM\(_{10}\) fraction, while the fine fraction is enriched with elements related to combustion processes (Zn, As, and V). Obvious spatial variations were observed in the ambient levels of elements, all the element concentrations in PU and KT sites have high levels than in HT site. The vicinity of major emission sources for PU and KT sites within the city lead to this phenomena. (Only winter PM\(_{10}\) Mg has high contents). Most elements in PM\(_{10}\) and PM\(_{2.5}\) have lower levels in summer than in winter among the three stations, except the concentrations of V in PM\(_{2.5}\). The decrease of these metallic elements in the summer period is essentially due to the washout effect of rainfall and to a better dispersion of the source emissions.

3.5. Chemical mass closure of particulate matter in Hong Kong

Mass closure for particles has become the accepted method for analysis of aerosols (Ma et al., 2001; Bardouki et al., 2003). Mass closure allows for source reconciliation, quality assurance, health and welfare impacts, and mitigation efforts with a high degree of confidence that major factors have not been ignored (Ma et al., 2001).

Sulfate, nitrate, ammonium, OC and EC are the major constituents in particles especially in PM\(_{2.5}\) collected at PolyU and KT. The major constituents of PM\(_{10}\) in HT are sulfate, nitrate, chloride, sodium and OC.

It is possible to estimate the mass concentration of fine particles by the following equation, assuming that all aerosol species accounted for significant fraction of the mass are measured. In this study, the aerosols can be classified into seven major types: crustal matter, sea salt, ammonium, sulfate, nitrate, elemental carbon and organic matter.

3.5.1. Crustal matter

Crustal matters originate from soil, and fugitive dust. Aluminum (Al) is usually selected as a tracer material of crustal elements (quartz filters are used in this study and therefore Si cannot be used as a tracer material). The concentration of Al in a surface of soil sample collected from HT was measured by Cheng et
al. (2000). The crustal matter concentration was estimated to be [Al]/7.26%.

3.5.2. Sea salt

The soluble Na in the aerosol samples is assumed to come solely from sea salt. Therefore the mass of sea salt is estimated by: Sea salt = 2.54 soluble Na.

3.5.3. Ammonium and sulfate

Secondary aerosols can exist in different chemical forms, including sulfate and nitrate salts. For simplicity, \((\text{NH}_4)_2\text{SO}_4\) is assumed to be the main form of secondary sulfates in urban environment. Therefore the measured mass of soluble ammonium and sulfate are included in the mass closure analysis.

3.5.4. Nitrate

Ammonium nitrate and sodium nitrate are the main form of secondary nitrates. In Hong Kong, sodium nitrate is the major form of secondary nitrates. Only the measured mass of soluble nitrate is included in the mass closure analysis.

3.5.5. Elemental carbon

Elemental carbon originates mainly from emissions from vehicular exhausts and combustion processes. The mass of elemental carbon in the samples is determined by TOR method measurement.

3.5.6. Organic matter

Since the chemical composition of the organic fraction of aerosol is largely unknown. In the literature conversion factors 1.4 is generally used (Turpin and Lim, 2001): organic matter = 1.4 * OC.

The factor of 1.4 corrects the organic carbon mass for other elements associated with the organic carbon molecule.

The yearly average percentage attributions of PM\(_{2.5}\) and PM\(_{10}\) to each of the seven aerosol types were given in Fig. 6. The sums of all included components are 71–79% for PM\(_{10}\) and PM\(_{2.5}\) among the three stations. In general, the PM\(_{2.5}\) samples are low in crustal matter and sea salt, and high in secondary sulfates and combustion products. On average the major components in the urban area were organic matter (>20%), sulfate (>16%) and EC (>8%). Vehicular, residential and industrial emissions were the main sources for the organic matter. Due to the proximity of the station to the seashore, sea salt was the major component in the PM\(_{10}\) fraction of HT. However sulfate was the major component in PM\(_{2.5}\) of HT due to transportation from northeast area. It should be noted that water content was not included. The unexplained mass (others) could be moisture (around 8%, ERDC, 1995), nitrates vaporized as nitric acid during storage, and unaccounted species. Also the organic matter is underestimated by using 1.4 as the conversion factor if WSOC contributed a large fraction in the particulate matter.

Recent studies found that an important fraction of total carbon shows chemical properties similar to those of natural humic and fulvic acids (Zappoli et al., 1999; Havers et al., 1998). Therefore, the masses of WSOC and water-insoluble organic carbon (WIN-
SOC) (WINSOC=OC – WSOC) could be converted to those of water-soluble organic substances (WSOS) and water-insoluble organic substances (WINSOS) separately. So far, the uncertainty in this calculation was that only estimated carbon-to-mass conversion factors have been applied (Gray et al., 1986; Zappoli et al., 1999). Recently, a solid phase extraction procedure has developed, allowing a conversion factor for the WSOS fraction to be experimentally be determined (Varga et al., 2001). The value of 1.9 was found for both the JFJ (Krivacsy et al., 2001) and the K-puszta aerosol (Kiss et al., 2002). This value is significantly higher than the estimated values used previously, and is in agreement with the value that has recently been recommended by Turpin and Lim (2001). For calculation of the WINSOS mass fraction the estimated value of 1.4 was used, but Kiss et al. (2002) found that this value may also be higher at rural and remote locations.

Thus 5 sets of samples (1 set=PM$_{2.5}$ and PM$_{10}$ samples) were selected from each site for winter and summer periods, and a total 60 samples were analyzed for WSOC (Ho et al., submitted for publication). The results of reconstructed chemical compositions in winter and summer using WSOS and WINSOS instead of organic matter were shown in Tables 4 and 5. The total organic substances (WSOS+WINSOS) increased about 2–6% of PM$_{2.5}$ and PM$_{10}$ mass fraction in both seasons when compared with using organic matter (1.4 * OC). At HT site, the percentage of WSOS was higher than WINSOS; while at urban sites, the percentage of WINSOS was higher then WSOS. HT, being a background site, is impacted by long-range transported aerosols that tend to more polar. The new results of chemical mass closure were summarised in the Tables 4 and 5. The total water-soluble fractions (inorganic+organic) accounted over 50% of the total aerosol mass for PM$_{2.5}$ among the three stations and PM$_{10}$ in HT during winter period. Besides anthropogenic emissions, transportation of secondary pollutants from mainland China was the major source in winter period.

On average, sulfate (>19%), WINSOS (>14%) and crustal matter (>11%) are the major components in the PM$_{10}$ samples in urban area during winter period. And sulfate (>25%), WINSOS (>15%) and WSOS (>11%) are the major components in the PM$_{2.5}$ in the urban area during winter period. But in the summer, the contributions of sulfate and crustal matter decreased while and the contributions of EC and WINSOS increased (>12% and 16% respectively). However at HT, the major components of PM$_{10}$ during winter are: sea salt (25%), sulfate (18%) and crustal matter (9%) while the major component for PM$_{2.5}$ during winter is: sulfate (31%), WSOS (12%) and WINSOS (9%). Better results were obtained for the chemical mass closure analysis in winter than in summer. In this study, no RH conditioner was used during sampling. However because of the high RH in Hong Kong, water contents may be one of the components found in the filters (especially in 20.3 $\times$ 25.4 cm quartz filters), which is especially significant during summer season (higher RH). We suggest that it is for this reason a large percentage of unresolved mass (others) was observed during the summer. In addition, at HT the conversion factors of

<table>
<thead>
<tr>
<th>Site</th>
<th>PolyU</th>
<th>KT</th>
<th>HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{10}$</td>
<td>PM$_{2.5}$</td>
<td>PM$_{10}$</td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Crustal matter</td>
<td>11.54</td>
<td>4.43</td>
<td>11.36</td>
</tr>
<tr>
<td>Sea salt</td>
<td>7.86</td>
<td>3.24</td>
<td>11.72</td>
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<tr>
<td>Ammonium</td>
<td>4.52</td>
<td>6.20</td>
<td>4.61</td>
</tr>
<tr>
<td>Sulfate</td>
<td>19.04</td>
<td>25.37</td>
<td>21.57</td>
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<td>PM$_{10}$</td>
<td>PM$_{2.5}$</td>
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<tr>
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organic matter may also be higher than at urban stations due to the higher contributions of WSOC.

4. Conclusion

The spatial distributions of major aerosol species in Hong Kong aerosol during winter and summer were characterised. Generally speaking, high concentrations of OC, EC (except in PolyU), water-soluble ions and elements were observed in winter among the three sampling sites for both PM$_{10}$ and PM$_{2.5}$ fractions. But at HT a significant difference was found. The highest concentration of EC was observed at PolyU roadside station in both winter and summer period due to the nearby vehicular emissions. The concentrations of sulfate and nitrate at HT in winter and summer were only slightly lower than urban areas. This may be caused by the long-range transportation of sulfate and nitrate from mainland China. High concentrations of ammonium was observed in the winter and this is the result of low thermal decomposition rate of ammonium chloride and ammonium nitrate, and the long-range transport ammonium during this season. Several other factors could also affect the concentrations of chemical species in both fractions, namely dilution effect due to the increase in the mixing depth was found in summer; more rainy days in the summer which cause the particulate matters to be washed out in the atmosphere; and physical dispersion/transport which may be the cause for higher concentrations in the winter. The prevailing winds in Hong Kong are north-easterly, especially in winter time, thus the transport of pollutants from the Asian Continent was one of the possible source for the background site. Clean marine air masses and wash out effects due to high precipitation both contribute to the low concentration in the summer.

Chemical mass closure calculations were done for PM$_{10}$ and PM$_{2.5}$ among the three monitoring stations. For reconstituting this gravimetric PM, seven aerosol types were considered: crustal matter, sea salt, ammonium, sulfate, nitrate, elemental carbon and organic matter. The major components in the urban areas were organic matter while sea salt and sulfate were the major components of PM$_{10}$ and PM$_{2.5}$ fraction of HT respectively. In order to achieve a better analysis organic matter should be divided into WSOS (WSOC * 1.9) and WINSOS (WINSOC * 1.4). High percentages of water-soluble ions were determined in the winter while high percentages of carbonaceous species were determined in the summer at the urban area. At HT the major components of PM$_{10}$ were sea salt, sulfate and crustal matter while the major component for PM$_{2.5}$ during winter is sulfate, WSOS and WINSOS. Better results were obtained for the chemical mass closure analysis in the winter. Under high RH, water contents may be one of the components in the filters (especially in 20.3 × 25.4 cm quartz filters). In addition, at HT background site the conversion factors of organic matter may also be higher than at urban stations due to the higher contributions of WSOC.

Acknowledgements

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References


Chan LY, Kwok WS. Roadside suspended particulates at heavily trafficked urban sites of Hong Kong—seasonal variation and dependence on meteorological conditions. Atmos Environ 2001;35:3177–82.


ERDC. Contributions of fuel combustion to pollution by airborne particles in urban and non-urban environments. Commonwealth
Lin JJ. Characterization of the major chemical species in PM$_{2.5}$ in the Kaoshuing City, Taiwan. Atmos Environ 2002;36:1911–20.