

APPENDIX 9

HONG KONG UNIVERSITY OF SCIENCE & TECHNOLOGY

WATER SOLUBLE ORGANIC COMPOUNDS

Chemical Characterization of Water Soluble Organic Compounds in Particulate Matters in Hong Kong

**A Final Report Submitted for the Provision of Service to the Environmental
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Submitted by

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Executive Summary

The Hong Kong Environmental Protection Department (EPD) has launched a study to understand the chemical characteristics of PM_{2.5} aerosols in Hong Kong. Three sampling sites, Mong Kok, Tsuen Wan, and Hok Tsui, were selected to represent roadside, urban, and rural environments in Hong Kong, respectively. Intensive sampling was carried out on a six-day cycle from November 2000 to October 2001 at the three locations. As part of this 12-month study, the work described in this report focuses on the chemical characterization of the water-soluble organic compounds (WSOC). Before chemical analysis, filter samples were combined together by season to produce four seasonal composites for each of the three sites. The major observations and conclusions are summarized below.

- The water-soluble organic carbon (WSOC) accounts for a significant portion of the total organic carbon mass, ranging from 14% to 64%. The highest WSOC contribution occurs in the fall composite at Hok Tsui, and the lowest in the summer composite at Mong Kok.
- Carbonaceous aerosol concentrations at Mong Kok are 2-3 times those at Tsuen Wan, which are more than 2 times those at Hok Tsui. Contrary to the stark spatial difference in the total carbonaceous mass, the water-soluble portion of the organic aerosols shows much reduced spatial variation. The WSOC concentrations are comparable in their concentration levels at the three sites. The same spatial trend is observed for the secondary inorganic aerosols (i.e., sulfate and nitrate). These observations seem to suggest that the WSOC fraction is mainly of secondary origin.
- The WSOC/OC ratio shows a clear spatial pattern, highest at Hok Tsui and lowest at Mong Kok. The OC/EC ratio also exhibits the same spatial pattern. Both observations indicate that the contribution of secondary organic aerosol is more prominent at the rural site.
- The water-soluble aerosol constituents are especially important in aerosol's role in visibility reduction because of their hygroscopic properties. Our measurements have shown that the water-soluble organic compounds account for a significant portion (18-32%) of the total water-soluble aerosol mass.
- The detailed chemical speciation work carried out so far has identified 12-29% of WSOC mass as organic anions, amino acids and aliphatic amines in free and combined form, carbohydrates, aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls.
- The organic anions detected include methanesulfonic and C₂-C₅ dicarboxylic acids. They account for 4-14% of the water-soluble organic carbon mass. Methanesulfonic acid has an oceanic origin. Oxalic acid is the most abundant organic acid species. It is found that the concentrations of other dicarboxylic acids correlate with those of oxalic acids, suggesting a common formation pathway. The lack of spatial variation in their concentration also suggests that secondary formation pathways are dominant sources.
- Amino acids are of biological origin. They account for 3-8% of the water-soluble organic carbon mass. The most abundant amino acids are glycine and valine. Three aliphatic amines, methylamine, ethylamine, and ethanolamine, are also present in all the samples. The aliphatic amines account for 0.3-0.6% of the WSOC mass. Their concentrations are

found to correlate with those of amino acids, indicating that aliphatic amines and amino acids likely originate from the same biological sources.

- The total monomeric carbohydrates are determined and their carbon mass contribution to WSOC is estimated to be 2-7%. One carbohydrate species, glycerol, is positively identified and quantified in the samples. Glycerol contributes to 0-14% of the total monomeric carbohydrates.
- Two aromatic acids, three hydroxy acids, two oxo-acids, and two dicarbonyls are identified in the aerosol samples. The nine compounds summing up together account for 0.7-3.2% of the water-soluble organic carbon mass. No discernible spatial variation is observed for these compounds, suggesting that they are most likely of secondary origin.

1 Introduction

Atmospheric particulate matter has been identified as a key pollutant in many major cities including Hong Kong. There is growing evidence of associations between fine particles smaller than 2.5 μm in diameter, called PM_{2.5}, and adverse health effects (NRC, 1998). In addition, PM_{2.5} is also a major contributor to regional visibility reduction (Watson, 2002). Characterization of the chemical composition of PM_{2.5} is an essential step to identifying toxicologically constituents. In addition, the chemical composition provides hints on the origins of the fine aerosols, since certain compounds are characteristic of specific sources. To formulate effective control strategies, policy-makers need to have knowledge of relative contribution from various PM_{2.5} sources.

The Environmental Protection Department (EPD) has launched a study to examine the chemical characteristics of PM_{2.5} aerosols in Hong Kong. Three sampling sites, Mong Kok, Tsuen Wan, and Hok Tsui, were selected to represent roadside, urban, and rural environments in Hong Kong, respectively. Intensive sampling was carried out on a six-day cycle from November 2000 to October 2001 at the three locations. Two co-located PM_{2.5} samplers at each sampling site collected aerosol samples every 24 hours on the first three days in the six-day cycle. Filter samples collected on day 2 were analyzed for mass, elemental composition, major soluble ionic species, and elemental and organic carbon concentrations. Filter samples collected on day 1 and day 3 were grouped into four seasonal composites. The organic carbon fraction of the composites samples was characterized at a molecular level.

As part of this 12-month study, the Hong Kong University of Science & Technology (HKUST) focuses on the chemical characterization of the water-soluble organic compounds (WSOC). More specifically, the goals are (1) to produce a chemical profile for the water-soluble organic carbon and investigate its seasonal and spatial variation in Hong Kong; and (2) to participate in data interpretation of the detailed chemical analysis of the organic carbon fraction.

2 Current status of characterization of organic carbon species in fine particulates

2.1 Solvent extractable organic species

Carbonaceous materials (organic substances and elemental carbon), could take up 20-80% of fine particulate mass (Jacobson *et al.*, 2000). Most often chemical speciation of organic carbon (OC) is performed on a fraction that extracts in relatively nonpolar organic solvents such as benzene, ether, hexane, or dichloromethane. The nonpolar organic solvent extractable mass typically accounts for only 50-60% of the total organic aerosol (Cass, 1998). Rogge *et al* (1993) have reported a detailed chemical speciation analysis of the organic solvent extractable fraction of ambient aerosols collected in the Los Angeles area. Using a combination of gas chromatography (GC) and derivatization techniques, they have analyzed ten classes of organics, i.e., alkanes, alkanolic acids, alkenolic acids, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, diterpenoid acids, polycyclic aromatic hydrocarbons (PAHs), n-alkanals, several N-containing compounds, and polyaromatic ketones and quinines. Among them, the dominant organics are alkanes and various acids (n-alkanoic acids, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, n-alkenoic acids, and diterpenoid acids). These organic compounds appear as resolved peaks on a GC chromatogram and they account for 76% of all the organics that appear as resolved GC peaks. Compared with the resolved peaks, a larger portion of organics appears as an unresolved

hump, called unresolved complex mixture (UCM). The UCM, albeit unresolved on a GC column, is well characterized. It consists of a large number of branched and cyclic hydrocarbons. In Rogge *et al.*'s study, the UCM and all the identified resolved peaks account for 49% of all the aerosol OC mass, leaving the remaining 51% un-characterized. Figure 1 summarizes the mass distribution of various aerosol components including organic constituents in the fine particles in Rogge *et al.*'s study.

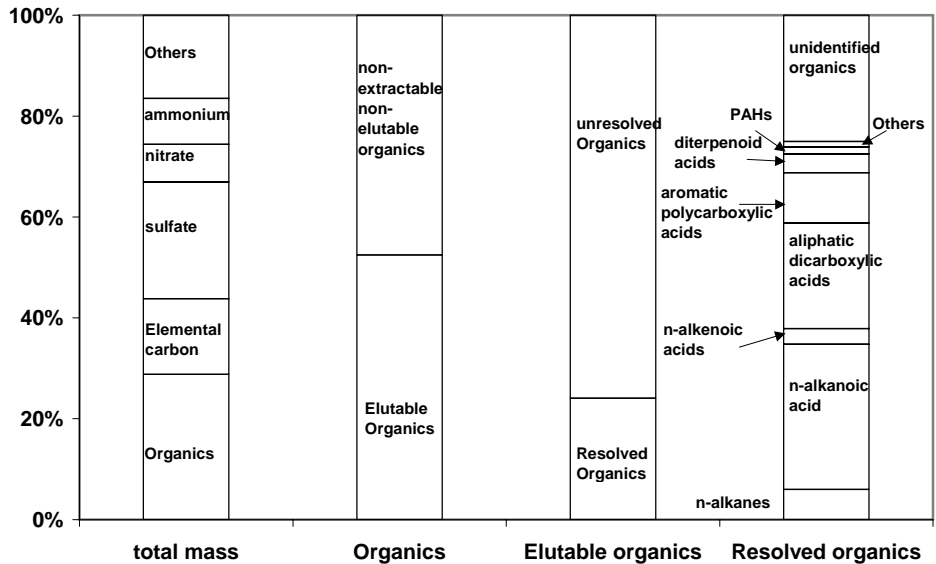


Figure 2-1. Mass balance on the chemical composition of annual mean fine particle concentrations at West Los Angeles in 1982. (source: Rogge *et al.*, 1993)

Zheng *et al.* (2000) have determined the concentrations of four classes of organic compounds, i.e., alkanes, fatty acids, alcohols and PAHs, in the methylene chloride extracts of PM_{2.5} aerosols collected from the HKUST campus. The sum of the measured species ranges from 56 to 234 ng/m³. The relative abundance of the four classes of compounds is shown in Figure 2.

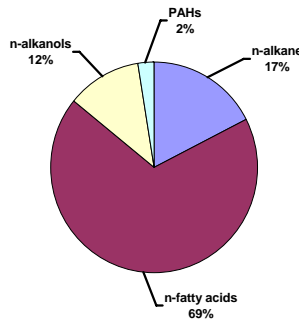


Figure 2-2. Annual mean relative abundance of four classes of organic compounds in Hong Kong's PM 2.5 aerosols (Source: Zheng *et al.*, 2000)

Fatty acids are the most abundant compounds among the four classes. Since the total aerosol OC was not determined in their study, it is not clear how much organic solvent extractable mass remains unidentified.

Measurements of nitrated PAHs in fine aerosols in Hong Kong were reported in a study by Xu and Lee (2000). The concentrations of nitrated PAHs range from 1 to 100 $\mu\text{g}/\text{m}^3$ with 1-nitropyrene as the most abundant nitro-PAH. This study indicates that nitro-PAHs are minor components in PM_{2.5} aerosols in Hong Kong.

Compared with organic speciation studies of PM_{2.5} aerosols, more studies have focused on the organic speciation of total suspended particulate (TSP) samples collected in the Pearl River Delta region. Zheng *et al* (1997) analyzed n-alkanes, n-fatty acids, n-alkanols and PAHs in TSP samples collected in six locations (Kwun Tong, Kwai Chung, HKUST, Mong Kok, Central-Western, and Hok Tsui) in Hong Kong in December 1993. The sum of all identified organic species accounts for 3-12% of the total aerosol mass extractable in methylene chloride. The Mong Kok location has the highest identified mass whereas the rural location Hok Tsui has the least fraction of aerosol mass identified. The higher fraction of identified organic mass at the Mong Kok location is mainly due to a much higher contribution from n-fatty acids to the total extractable aerosol mass. Fang *et al* (1999) compared the characteristics of the above four classes of compounds in TSP samples collected before and during the dust episode of 9-10 May 1996. They demonstrated the usefulness of organic speciation in identifying aerosol sources. Zheng and Fang (2000) made measurements of PAHs in TSP samples at six locations in Hong Kong from 1993 to 1995. They observed distinct spatial and seasonal variability, which can be explained by the synoptic meteorological conditions in Hong Kong. Simoneit *et al* (1991) reported the chemical composition of the solvent extractable aerosol mass in two TSP samples collected in Guangzhou in March 1988. Among the targeted organic species are alkanes, PAHs, n-fatty acids, n-alkanols, n-alkanones and diterpenoid acids. The sum of the above organic compounds contributed to 12% and 62% of the solvent extractable aerosol mass in the two samples.

Speciation of the organic solvent extractable fraction permits the calculation of several parameters for differentiation of biological and anthropogenic organic aerosol sources. This fraction of organics mainly comes from microbial and vascular plant lipids, petroleum hydrocarbons, and incomplete combustion of fossil fuels. Speciation analyses yield concentrations of individual alkanes, PAHs, fatty acids and n-alcohols. Consequently, two parameters characteristic of aerosol sources, carbon preference index (CPI) and carbon number maximum (C_{max}) for homologs, can be calculated.

Both CPI and C_{max} are measures to differentiate anthropogenic and biogenic sources. The CPI for alkanes is expressed as the ratio between the total mass of the odd homologs and that of the even homologs. The CPI for fatty acids and n-alcohols is the same ratio only inverted to have even-to-odd homologs. In biological derived particles, odd alkanes are predominant over even alkanes because highly specific enzyme-regulated biosynthetic processes yield the discrete structural component of odd carbon numbers. Simoneit (1986) has shown (1) n-alkane CPI values of 6-30 for plant wax distributions; (2) CPI values of 10 for natural forest fires; (3) CPI values of 1.2-5 for slash burns; (4) CPI values of 0.96-1.01 for petroleum products (*e.g.* total crude oil, diesel fuel, and lubricating oil). CPI values greater than 3 indicate that the n-alkanes observed are from predominantly biological materials, and that CPI values near unity signify the presence of n-alkanes derived from petroleum products or from the partial thermal alteration (*i.e.* incomplete combustion) of petroleum.

C_{max} is the carbon number of the compound that has highest abundance among its homologs. C_{max} lends supportive evidence for the relative contribution of biological and anthropogenic sources. For example, an alkane C_{max} value at C_{29} indicates a significant contribution from biological sources; a fatty acid C_{max} value at C_{16} indicates a significant contribution from microbiological sources. A comprehensive summation of the characteristic C_{max} values for various sources has been given by Simoneit (1986).

Another useful measure is the ratio between UCM and n-alkanes. Petroleum contributes to the observation of UCM, which comprises of branched and cyclic hydrocarbons. The ratio between UCM : n-alkanes may indicate the degree of contribution from petroleum and natural sources. The natural hydrocarbons derived from higher vascular plants exhibit no UCM hump, and this ratio is <1 (Simoneit and Mazurek, 1986). Values >2 reflect significant contribution from petroleum products (Simoneit, 1986).

2.2 Water-soluble organic compounds

A number of studies have shown that water-soluble organic compounds constitute a significant fraction of carbon mass. As shown in Table 1, studies encompassing both urban and rural locations have reported that water soluble organic carbon accounts for approximately 20% to 67% of the total particulate carbon in the atmosphere (Decesari *et al.*, 200; Sempere and Kawamura, 1994; Muller *et al.*, 1982, Cadle and Groblicki, 1982). Our recent studies have revealed that the WSOC accounts for on average 28% and 47% of the carbon mass in fine particles at a coastal site in Hong Kong during summer and winter time, respectively (Yu, 2001).

Table 2-1. Water-soluble fraction of atmospheric particulate organic matter

Investigators	Location	Sample	Time period	WSOC/TC	# samples
Decesari <i>et al.</i> , 2000	N. Italy	PM1.5	1996	55%	1
Sempere and Kawamura, 1994	Tokyo	TSP	1992	28-55%	4
Cadle & Groblicki, 1982	Denver, CO	TSP	1978	27±12%	6
Mueller <i>et al.</i> , 1982	LA, U.S	TSP	1977-78	30-67%	96
Mueller <i>et al.</i> , 1982	2 urban and 7 nonurban locations in northeastern US.	PM2.5	1977-78	20-60%	18 per location
Yu, 2001 ^a	Hong Kong	PM2.1	Jul-Aug, 2000	28%	3
Yu, 2001 ^a	Hong Kong	PM2.5	Feb., 2001	27-61%	11

^a: Samples were taken at the HKUST campus, which is located at the eastern coast and further away from commercial and industrial activities.

The WSOC composition remains poorly characterized. Observations regarding the molecular composition of the water-soluble organic fraction are limited. Available studies on characterizing WSOCs have mainly aimed at organic anions, dicarboxylic acids, keto acids and dicarbonyls. Kawamura and his colleagues, for example, have studied water-soluble organics including α,ω -dicarboxylic acids (C_2-C_9), ω -oxo-carboxylic acids (C_2-C_9), pyruvic acid, and α -dicarbonyls (C_2-C_3) in urban aerosols as well as Antarctic and Arctic aerosols (Sempere and Kawamura, 1994; Kawamura *et al.*, 1996a, b). They employed water extraction, followed by analysis of the above chemicals as their dibutyl ester using a gas chromatography/mass spectrometry (GC/MS). The above compounds account for only 5-17% of the total water-soluble organic carbon in the urban aerosols collected in Tokyo. For the

Antarctic and Arctic aerosols, no measurement was carried out on the total WSOC fraction. Consequently, the relative contribution of these species to the WSOC was unknown. Li and Winchester (1993) measured eight water-soluble organic anions--formate, acetate, oxalate, propionate, methanesulfonate, lactate, benzoate, and pyruvate--in Arctic aerosols using ion chromatography (IC). In a later study, Li *et al* (1996) measured a selected number of WSOCs including glyoxylic acid, and five organic anions (formate, acetate, propionate, oxalate, and methanesulfonate) in aerosol samples collected near the coast of Southern Nova Scotia, Canada. The total WSOC mass was not determined in either study, therefore it is unknown how much organic anions and glyoxylic acid contribute to the total WSOC fraction.

Candidate water-soluble organic compounds have been identified on the basis of their solubility, condensibility, and atmospheric occurrence by (Saxena and Hildemann, 1996). They include organic anions, dicarboxylic acids, oxo acids, dicarbonyls, carbohydrates, amino acids, aliphatic amines, urea, and some miscellaneous multifunctional compounds containing multiple hydroxy, carboxyl, and carbonyl groups (*e.g.* glyceraldehyde, malic acid, citric acid, lactic acid, and tartaric acid).

The chemical composition of the WSOC fraction is still largely unknown. Speciation work offers us insight into the sources of this often overlooked fraction of organic materials. For example, glycerol, a C₃ sugar alcohol, is soluble in water and known to be associated with cooking activities (Nolte *et al.*, 1999). Low-molecular weight dicarboxylic acids and ketoacids, also soluble in water, have major contribution from secondary sources (Kawamura and Gagosian, 1987).

3 Seasonal division and episode identification*

3.1 Summary

The sampling period, 1 November 2000 – 31 October 2001, is divided into the following seasons:

Winter:	November 12, 2000	–	March 13, 2001
Spring:	March 17, 2001	–	May 16, 2001
Summer:	May 19, 2001	–	September 20, 2001
Fall:	September 21, 2001	–	October 31, 2001

The days that fall between seasons are transitional periods, ranging from 2 to 5 days. Samples taken on these days have been archived and excluded from the detailed chemical analyses. The fall season in 2000 overlapped with the sampling period for a few days, *i.e.*, from November 5 to 11, 2000. Samples taken on these days do not provide enough aerosol materials for trace organic analysis. They are also archived and excluded from the seasonal composite samples.

Three pollution episodes are identified as:

Dust episodes:	8-11 March 2001	and	12-16 April 2001
O ₃ episode:	14-19 September 2001		

* This section is prepared together with Dr. Alexis K. H. Lau, Center for Coastal and Atmospheric Research, Hong Kong University of Science & Technology.

3.2 Seasonal division

Hong Kong is situated in the sub-tropics along the southeast coast of China. The seasonal evolution of weather in Hong Kong is closely related to and controlled by seasonal evolution of the East Asian Monsoon system.

During the summer, a large surface low-pressure system develops over Asia (with center over the Tibetan Plateau) in response to rising surface temperature over the continent. In association with this continental scale low-pressure system, winds flows cyclonically (in the counter-clockwise direction) into the Asian landmass in the lower levels, rises up over the continent, and flows out of it anti-cyclonically (in the clockwise direction) in the upper levels.

During the winter, the temperature over the surrounding tropical oceans is much warmer than that of the Asian continent, and hence the center of rising motions shifts southward over the oceans, inducing lower surface pressure over the oceans and higher surface pressure over the continent. In response to this changed temperature and pressure patterns, the flow pattern over the Asian continent are characterized by surface winds flowing anti-cyclonically out of the continent towards the equatorial pressure trough, and the upper-level winds becoming mostly westerly (as part of the outflow of the equatorial convections).

Many have argued that there are only two seasons over the monsoon regions – the wet (summer) and the dry (winter) season. The transition periods (spring and fall) between them are much shorter. Typically, the summer phase of the Asian monsoon extends from May to September and the winter phase extends from November to March. Spring (or the transition from winter to summer) generally occurs around April from late-March to early-May and fall (the transition from summer to winter) occurs around October from late-September to early-November.

In this report, *sea-level pressure* and *upper-level wind direction* are used to show the typical seasonal change around Hong Kong. Surface winds are not useful for depicting the seasonal variations because boundary layer effects (not related to the seasons) are strong near the surface, and they tend to obscure the seasonal variations of the surface winds.

- Sea-level pressure around Hong Kong

Sea-level pressure (SLP) around Hong Kong fluctuates in phase with the East Asian monsoon, lower in summer and higher in winter. This seasonal variation can be clearly seen in Figure 3-1a, which shows the SLP variations at a weather station in Shenzhen (WMO station number 59493) between 1 May, 1997 and 31 October, 2001.

- Direction of Upper Level Wind

The direction of upper level winds is one of the best indicators for seasonal change around Hong Kong. During the summer, the center of strong rising motion of the Asian monsoon complex is to our northwest over the Tibetan Plateau area. Associated with the upper-level anticyclonic (clockwise) outflow of the strong monsoon convections, a strong easterly current is established over the south / Southeast Asian sector (including Hong Kong) near the top of the troposphere during the summer months. In contrast, during winter, the

center of rising motion shifts southward to the equatorial region, and the upper level flow in the east / southeast Asian sector (including Hong Kong) is dominated by westerlies.

This seasonal variation can be clearly seen in Figure 3-1b, which shows the variations in wind directions over a weather station in Hong Kong (King's Park, WMO station number 45004) between 1 May, 1997 and 31 October, 2001. This figure showed clearly that the upper-level winds over Hong Kong are easterly during the summer and westerly during winter. The wind directions are more variable during the transition periods of spring and fall.

A rough division of the study period (1 November 2000 – 31 October 2001) into four seasons can be made by examining in finer details at the time evolution of the upper-level wind directions (Figure 3-2). We can roughly divide the study period into winter (mid-November 2000 to mid-March 2001), spring (mid-March to mid-May), summer (mid-May to the end of September) and fall (late September and October 2001; and also early November 2000).

The next step is to pinpoint the exact dates of the seasonal divisions. Atmospheric scientists usually define the arrival date of an individual season as the arrival date of the first *synoptic event* that is typical in the respective seasons. For example, cold surges are common in the winter and hence the arrival of the first cold surge event is used to identify the start of the winter season. Hence, to define the exact dates for the seasonal divisions, it is useful to look for rapid changes of the relevant parameters (*e.g.* SLP and dew point) in the division vicinities identified in the aforementioned paragraph.

Figure 3-3 shows the time variation of SLP from 1 April 2000 to 23 October 2001. Four periods are selected for a closer examination of the exact date of the seasonal transitions. The detailed variations of SLP and dew point for these periods are plotted as different panels in Figure 3-4.

Figure 3-3 shows a gradual rising trend of SLP from mid-October to mid-November, and then the SLP remained high for a few months. A more detailed plot in Figure 3-4a shows that the SLP started a rapid increase on 6 November and reached a local maximum on 12 November. Afterwards, the SLP fluctuated but remained high for a few months. In addition, there was also a sharp drop in dew point corresponding to the SLP increase from 6 to 12 November. Such concerted changes in SLP and dew point are indicative of the arrival of cold air mass from the north during winter cold surge events. On the basis of the above analysis, 6 November is suggested as the end-date of fall 2000, and 12 November is suggested as the beginning date for winter 2000.

The same analysis was carried out for the period marking the end of the winter. The SLP had a sharp decrease from 13 to 16 March 2001 whereas the dew point saw a rapid increase during the same period (Figure 3-4b). These changes are indicative of the arrival of warm and moist air mass, which signaled the beginning of transition period (spring). Hence, 13 March is suggested as the end date of winter 2000/2001 and 17 March is suggested as the beginning of spring.

Similarly, the transitional periods for the start and the end of the summer were examined (Figure 3-4c and Figure. 3-4d). The division dates were accordingly identified.

3.3 Dust episodes

In a dust episode, RSP levels are expected to be high across the territory. However, high RSP levels may result from a dust event or local sources. The main contributing local sources are combustion sources including vehicular traffic, which correlate to CO or NOx levels. By examining both RSP and CO /NOx levels, it is possible to differentiate a dust event and local emission sources.

Figure 3-5 identifies a dust event from 8 to 11 March using Tai Po and Tap Mun as examples. Table 3-1 summarizes the daily maximum RSP concentrations at Tai Po and Tap Mun for this period. High RSP concentrations were measured in Beijing and Shanghai just one to three days before the onset of the RSP surge in Hong Kong. This trail of high RSP concentrations again indicated that this high RSP episode was a dust event.

A second dust episode was from 12 to 16 April. Figure 3-6a shows the RSP and CO concentration profiles at Tap Mun for this period. It is clear from Figure 3-6a that during 12-16 April, RSP levels surged while CO did not show such an increase. Air mass back trajectory analysis also shows the long-range transportation of the air mass from the north before arriving at Hong Kong on 16 April (Figure 3-6b). Visibility data supported the occurrence of this dust episode (See Appendix 3-1). The visibility degradation was evident when comparing the visibility before and after the arrival of the dust storm. The visibility maps of the entire China and its surrounding areas for this period also show the dust movement direction. Dust in this episode crossed the Pacific Ocean and reached North America. Satellite images have captured the dust trail and were widely reported in the mass media (See the Appendix 3-1).

Table 3-1. RSP Concentrations at Two Rural Sites during a Dust Event

Date	RSP max (ug/m3)		
	Tai Po	Tap Mun	
3/5/01	129	132	
3/6/01	143	134	
3/7/01	147	108	
Dust event {	3/8/01	136	146
	3/9/01	190	188
	3/10/01	159	139
	3/11/01	161	101
3/12/01	72	81	
3/13/01	93	100	

3.4 Ozone episode

Characteristics of ozone episodes include low wind speed, strong solar radiation and high ozone concentrations at rural sites. An ozone episode has been identified to occur between 14 and 19 September 2001 based on the above characteristics. Table 3-2 lists the ozone concentrations during this episode at two rural sites, Tung Chung and Tap Mun. Figure 3-7 demonstrates the correlation between O₃ formation and solar radiation.

Table 3-2. Ozone Concentrations and Other Relevant Parameters at Two Rural Sites during an Ozone Episode.

date	wind speed	Tung Chung			Tap Mun	
		Daytime hourly ave. solar irradiation	O3 max	NO2 max	O3 max	NO2 max
		m/s	w/m2	µg/m3	µg/m3	µg/m3
9/11/01	20	31.5	98.4	72.0	129.0	12.2
9/12/01	12	48.5	140.1	98.1	102.9	27.4
9/13/01	9	51.1	155.4	117.1	115.6	13.7
9/14/01	11	52.0	212.1	205.9	247.7	63.2
9/15/01	12	51.1	348.1	192.1	160.3	102.8
9/16/01	9	62.1	227.8	147.2	160.1	83.7
9/17/01	10	57.4	194.2	161.5	287.9	78.2
9/18/01	11	58.3	244.4	158.3	190.3	53.4
9/19/01	12	53.3	324.8	171.8	135.0	74.6
9/20/01	17	31.2	150.7	110.9	123.3	51.7
9/21/01	26	14.0	105.6	64.5	119.8	2.6
9/22/01	19	61.6	121.5	94.6	133.9	8.1

Ozone episode

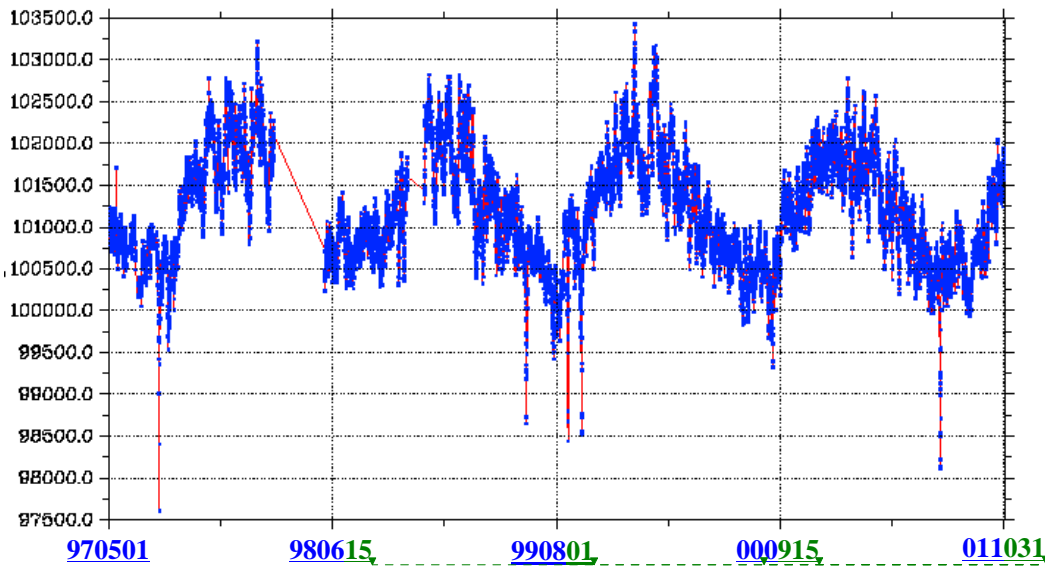


Figure 3-1a. Time-variations of the Sea level Pressure measured at Shenzhen from May 1, 1997 to October 31, 2001.

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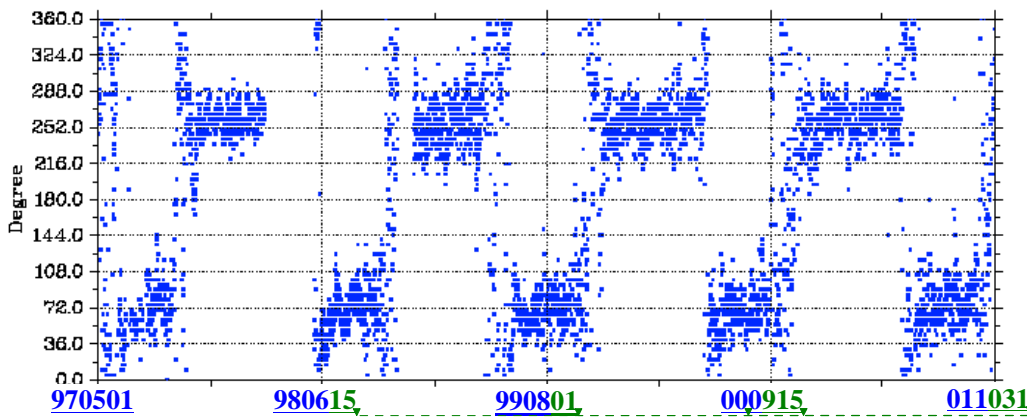


Figure 3-1b. Time-variations of the direction of upper level wind measured at ca. 20000 m at King's Park (Hong Kong) from May 1, 1997 to October 31, 2001.

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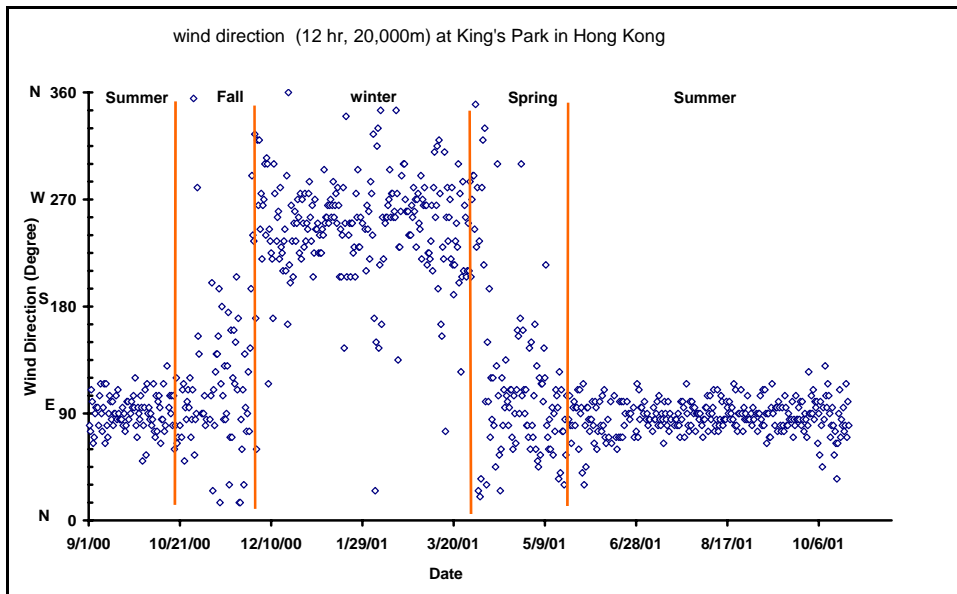


Figure 3-2. Time profile of wind direction at *ca* 20,000 m height over the course of one year (September 1, 2000 – Aug. 30, 2001) at the King's Park in Hong Kong.

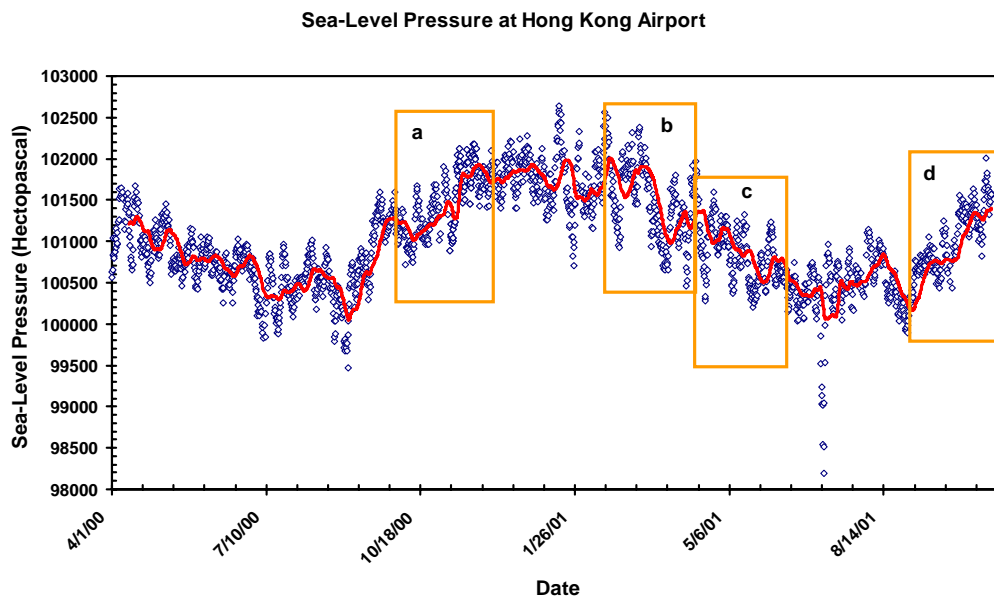
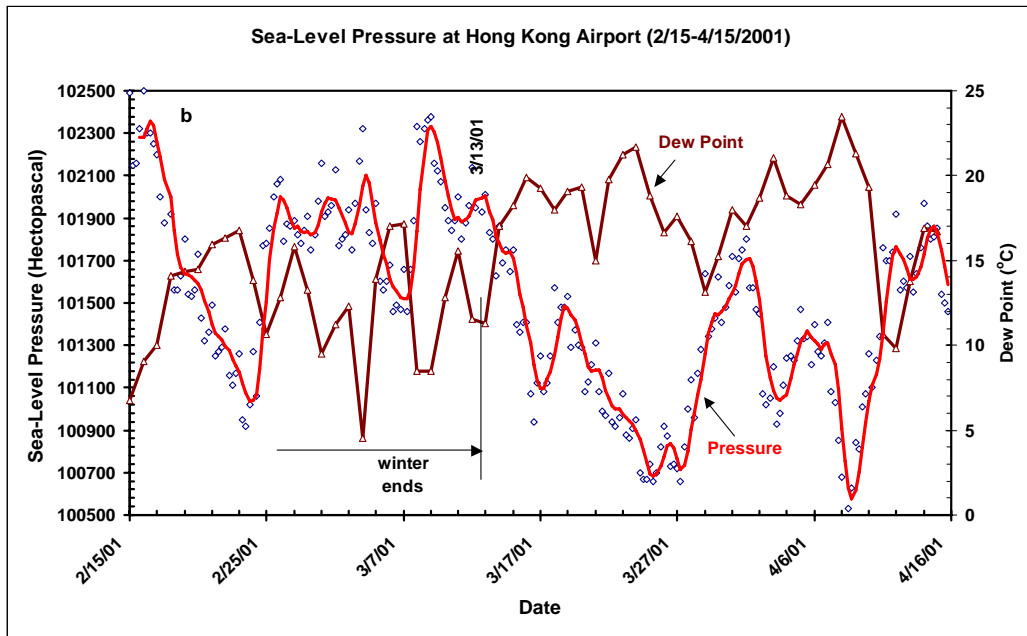
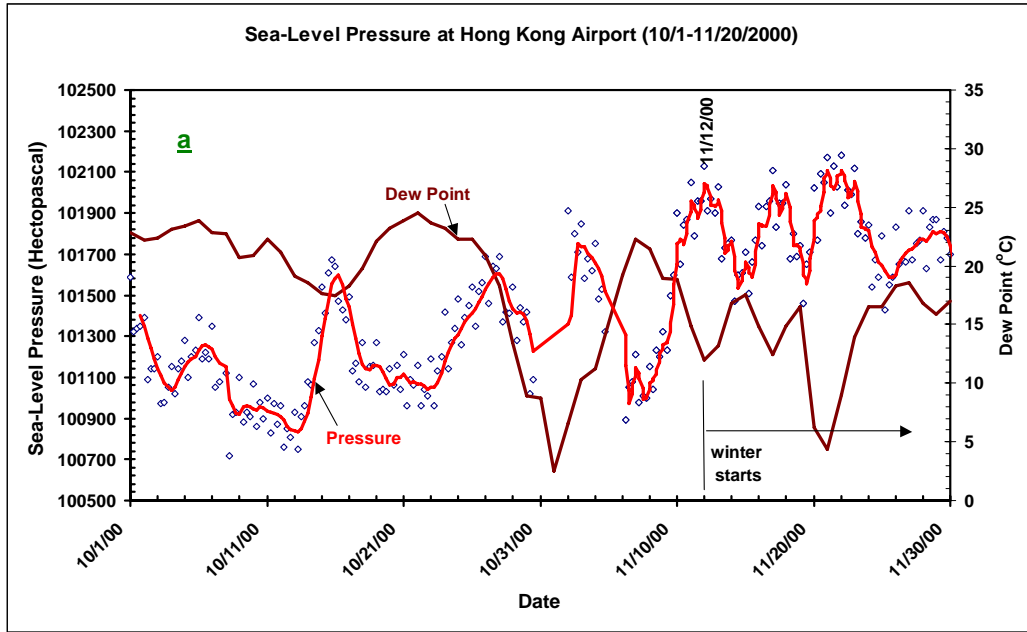


Figure 3-3. Sea level pressure at the Hong Kong Airport from 1 April 2000 to 23 October 2001. The details in the frames a, b, c, and d are plotted in Figure 3-4.



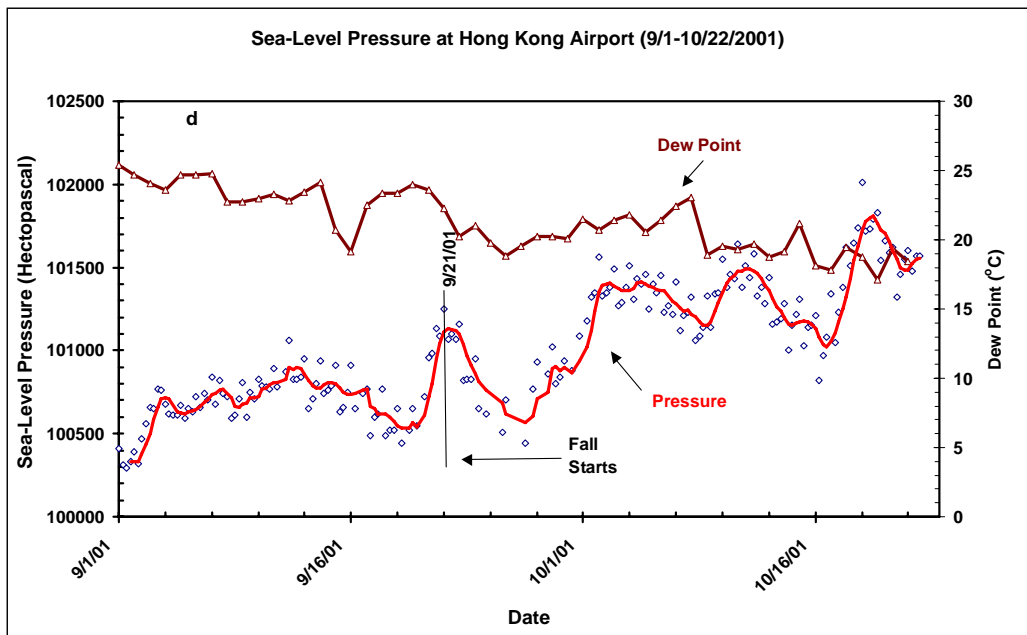
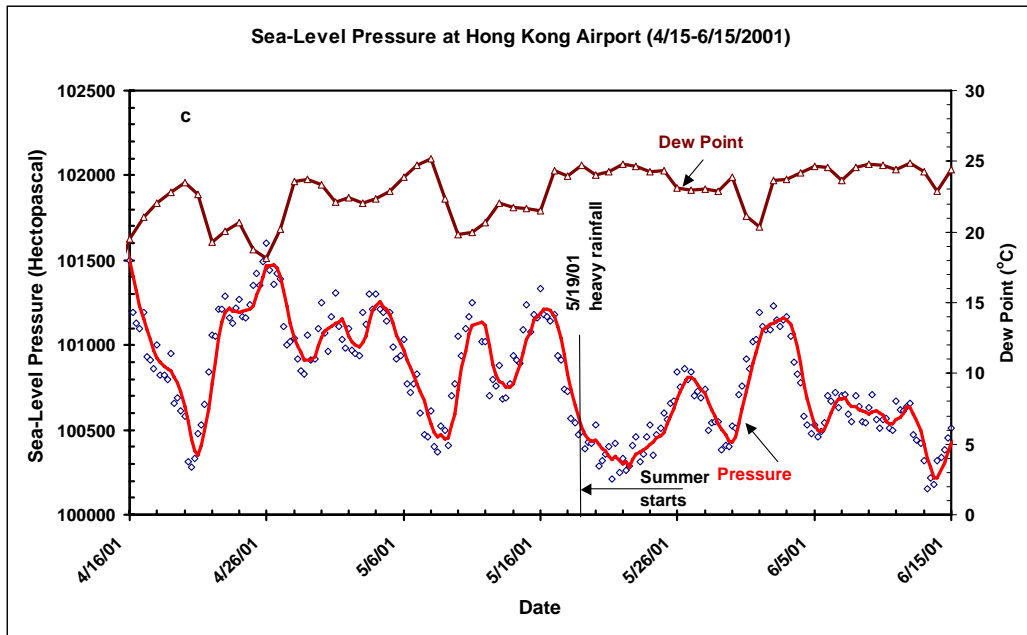


Figure 3-4. Sea level pressure and dew point at the Hong Kong Airport for the seasonal transition periods: (a) Oct. 1 – Nov. 20, 2000, (b) Feb. 15 – Apr. 15, 2000, (c) Apr. 15 – Jun. 15, 2001, (d) Sep. 1 – Oct. 22, 2001.

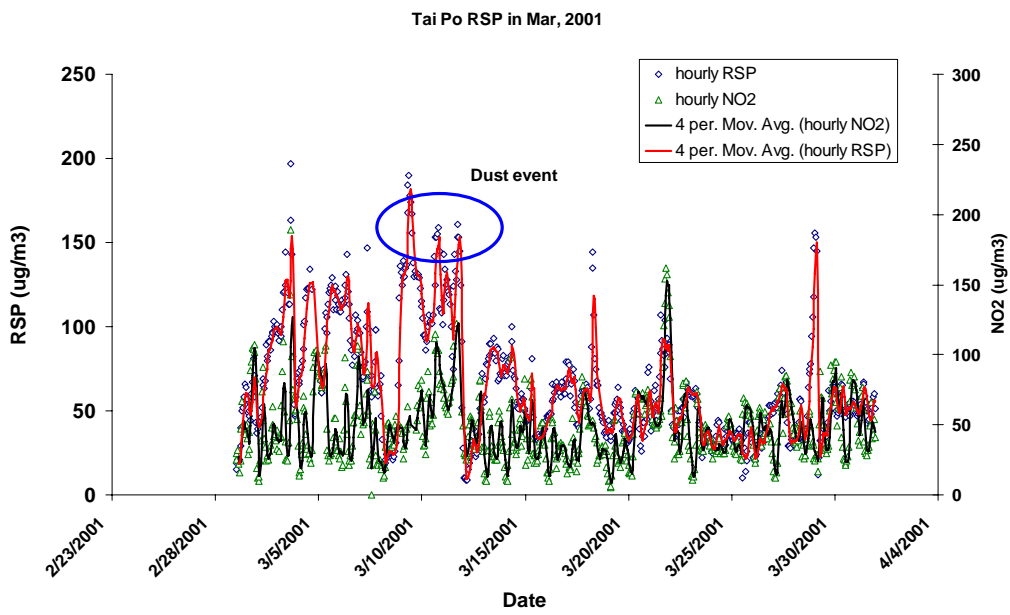
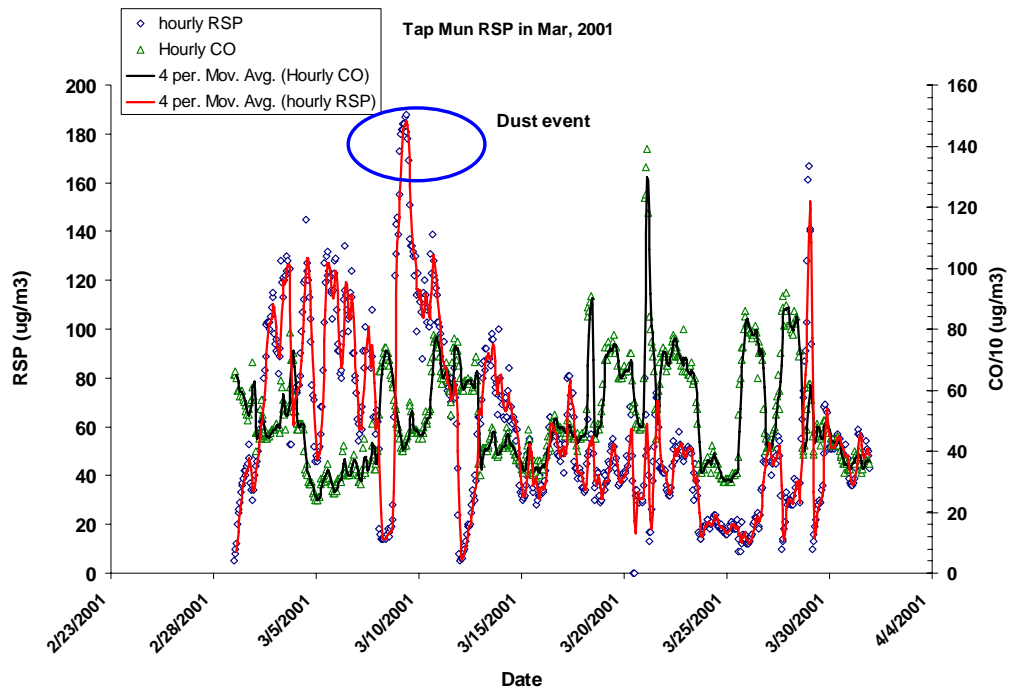


Figure 3-5. RSP concentration profiles at Tap Mun and Tai Po in March 2001.
 (4 per. Mov. Avg. denotes 4 periods moving average curve, which is plotted using the average points of 4 adjacent data.)

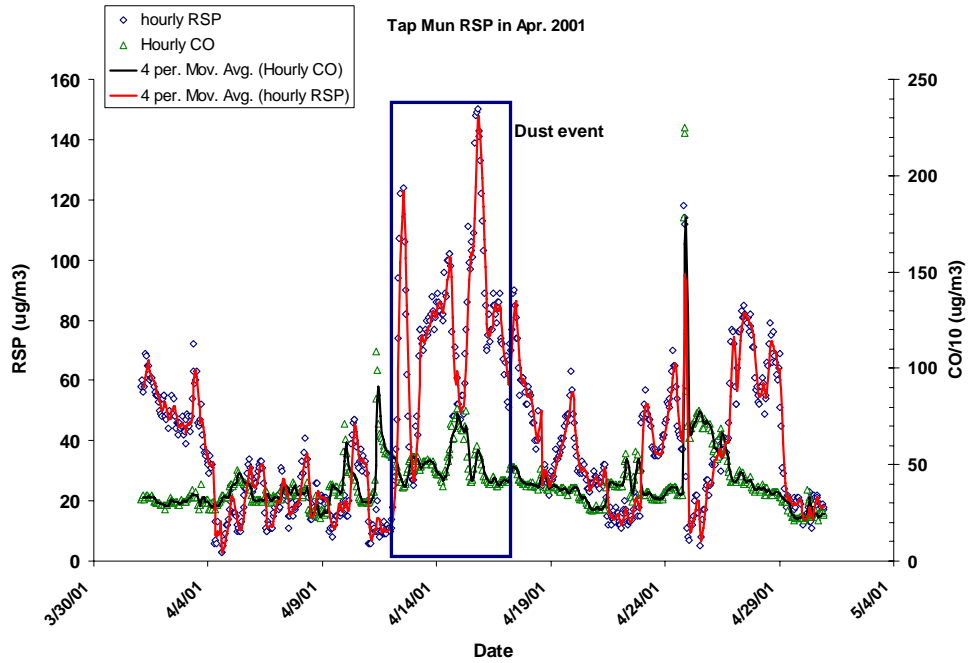


Figure 3-6a. RSP concentration profiles at Tap Mun in April 2001

(4 per. Mov. Avg. denotes 4 periods moving average curve, which is plotted using the average points of 4 adjacent data.)

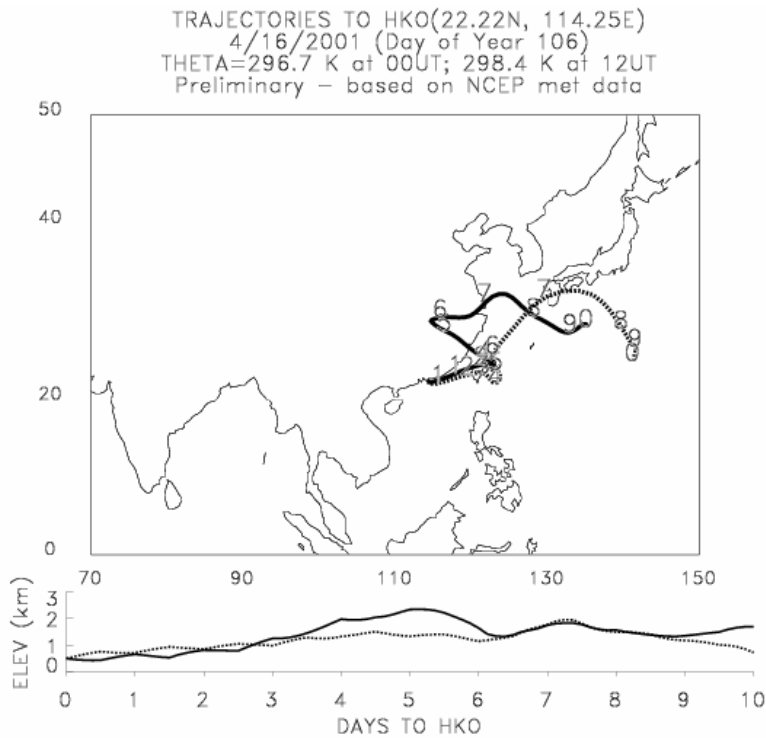


Figure 3-6b. Air mass trajectories before arriving at HK on 16 April 2001

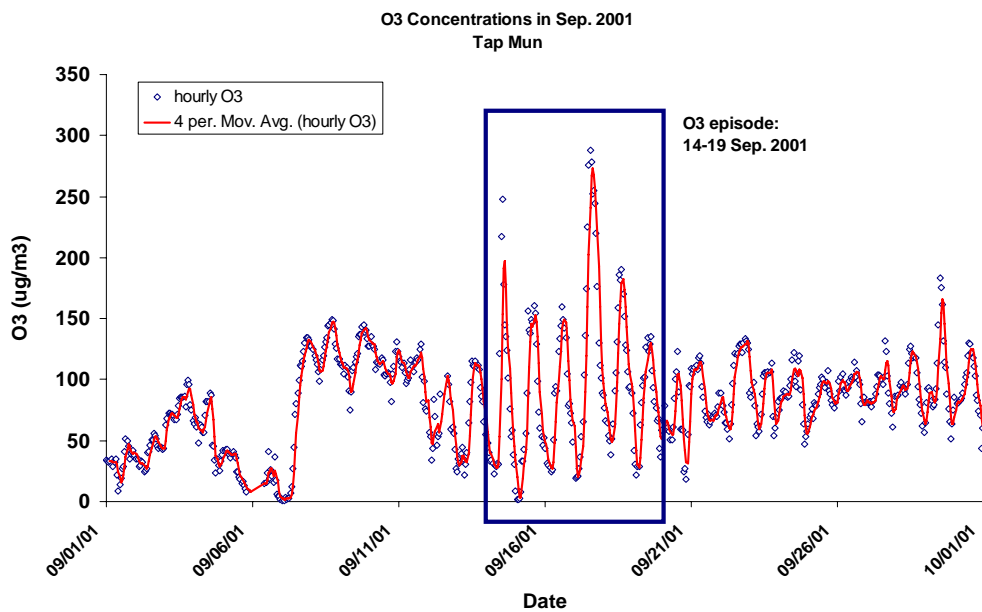
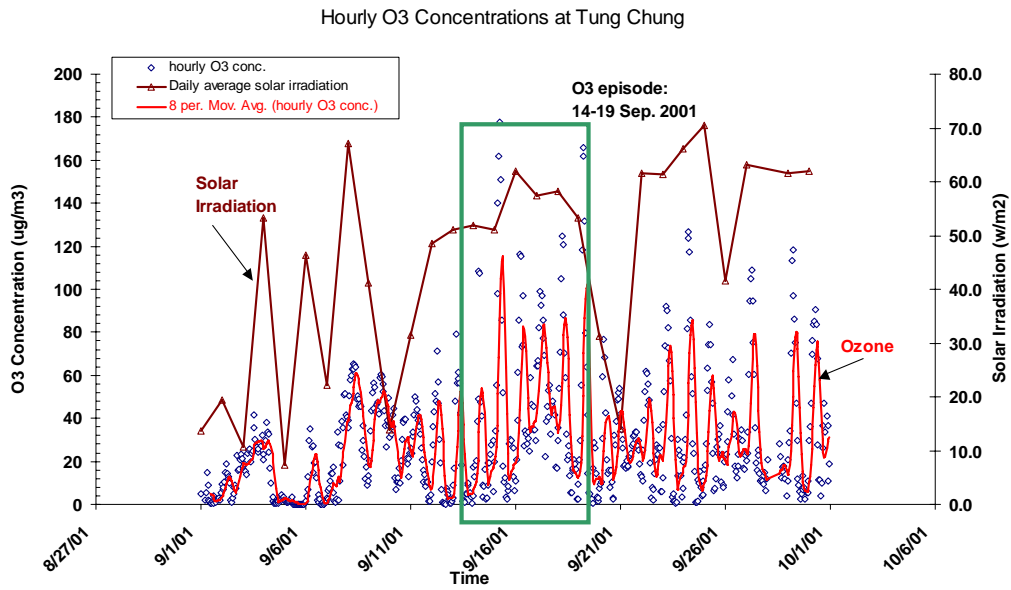


Figure 3-7. Ozone profiles at two rural sites.

(8 per. Mov. Avg. denotes 8 periods moving average curve, which is plotted using the average points of 8 adjacent data.)

4 Extraction and analysis scheme for chemical characterization of WSOC

4.1 Division and grouping of filters

Each day-1 and Day-3 filter was divided into four quarters using a filter cutter designed and fabricated by the mechanical workshop of HKUST. This cutter divides a 47-mm filter into equal quarters with a precision better than 3%, as determined by the mass value of each quarter. See Appendix 4-1 for the use and maintenance of the filter cutter.

The day-1 and day-3 filters were cut and distributed to the various participants of the project by the Government Lab. Our group received one quarter of each of the day-1 and day-3 filters. The quarter filters were grouped together by seasons, which were defined in section 3, before water extraction. The purpose of combining samples is to ensure enough aerosol materials for various speciation analyses and in the same time yield seasonal characteristics of the PM_{2.5} aerosols. Table 4-1 gives summary information of the seasonal composite samples.

Table 4-1. Summary information of the seasonal composite samples

composite	corresponding period	# quarter-filters per composite			Notes
		MK*	TW*	HT*	
Winter	12-Nov-2000 – 13-Mar-2001	79	76	80	exclude 11-Mar-2001 dust episode samples
spring	17-Mar – 16-May-2001	38	38	38	exclude 12 and 16-Apr-2001 dust episode samples
Summer	19-May – 20-Sep-2001	78	78	77	exclude 15 and 19-Sep-2001 O ₃ episode samples
Fall	21-Sep – 31-Oct-2001	26	26	26	

* MK, TW, and HT denote Mong Kok, Tsuen Wan, and Hok Tsui, respectively.

It was estimated that the episodic samples could provide enough materials for the determination of the total WSOC concentrations, but not enough for the detailed speciation work. As a result, no attempt was made to analyze the episodic samples.

4.2 Measurement of the total WSOC

The WSOC fraction is isolated from the rest of OC by water extraction of filter samples. The detailed procedure is given in Appendix 4-2. A brief description is given below. Each composite of quarter-filters are extracted with 100 ml of water, followed by concentration of the water extract to a final volume of 25 ml using a rotary evaporator.

Chemical analyses of the water extracts have included both determination of the total WSOC concentration and quantification of the individual components. With the total WSOC mass determined, it is possible to quantify the relative contribution of individual WSOC components to the total WSOC mass. The total WSOC are measured using an aerosol carbon analyzer by spiking the water extract of aerosol samples onto a clean filter strip. The standard operating procedure for the measurement of WSOC concentrations is described in Appendix 4-2.

4.3 Speciation of WSOC

The target individual compounds for speciation in the WSOC are limited by our knowledge of the possible components and available lab techniques. The following WSOC target components are selected for speciation analysis for the above reason.

1. Organic anions, examples: formate, acetate, oxalate, methanesulfonate, and *etc.*
2. Amino acids, examples: valine, glycine, and *etc.*
3. Aliphatic amines, examples: methylamine, ethylamine, and ethanolamine.
4. Carbohydrates, examples: monosaccharides and their derivatives such as reducing sugars, sugar alcohols, and sugar acids, *etc.*
5. Oxo-carboxylic acids (C₂-C₉): examples: glyoxylic acid, pyruvic acid, and *etc.*
6. Aromatic acids (C₂-C₉): examples: benzoic acid, phthalic acid, and *etc.*
7. Hydroxy acids: examples: lactic acid, glycolic acid, malic acid, and *etc.*
8. Dicarboxyls: examples: glyoxal and methylglyoxal.

Portions of the 25-ml water extract are allocated for the determination of the above components. Table 4-2 summarizes the measurement techniques. Details are described below and in Appendices 4-3, 4, 5, and 6.

Table 4-2. Summary of measurement techniques

Parameter	Measurement Technique
WSOC	Carbon analysis of water extract using an aerosol carbon analyzer
Organic anions	Ion Chromatography
Amines & amino Acids	Derivatization +HPLC/fluorescence detection
Total carbohydrate-like compounds	Chemical degradation to formaldehyde + Detection of formaldehyde by HPLC/PDA
Aromatic acids and hydroxy acids	Derivatization + GC/MS detection
Oxo-carboxylic acids and dicarboxyls	Derivatization + GC/MS detection

4.3.1 Organic anions

Organic anions are analyzed using ion chromatography. Appendix 4-3 describes the detailed analysis conditions. Individual organic anions often exist in aerosols at low concentrations. To maximize the detection limit, we have used an injection volume of 50 µl. An injection volume of 250 µl was also tried during method development. It was found that the large injection volume has caused peak broadening to such a degree that co-elution of lactate, acetate and, formate prevents their reliable quantitation. Together with organic anions, four inorganic anions, chloride, nitrate, sulfate, and nitrite, are also quantified.

4.3.2 Amino acids and aliphatic amines

These two classes of compounds share a common functional group, -NH₂. As a result, both can be analyzed using Waters' AccQ-Tag method (Cohen *et al.*, 1993). The amine group reacts with 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) to produce stable fluorescent derivatives that fluoresce strongly at 395nm (Figure 4-1). The resulting derivatives of various amino acids and aliphatic amines can be resolved on a HPLC column using gradient elution of three eluents: acetonitrile, water, and phosphate buffer.

Besides free amino acids, proteinaceous materials, which consist of two or more amino acid units, could be present in the ambient aerosols. For example, Likens *et al* (1983)

detected this kind of materials in rain samples. The proteinaceous materials can be regarded as combined amino acids and measured as their compositional amino acids through conversion to the free amino acids by hydrolysis.

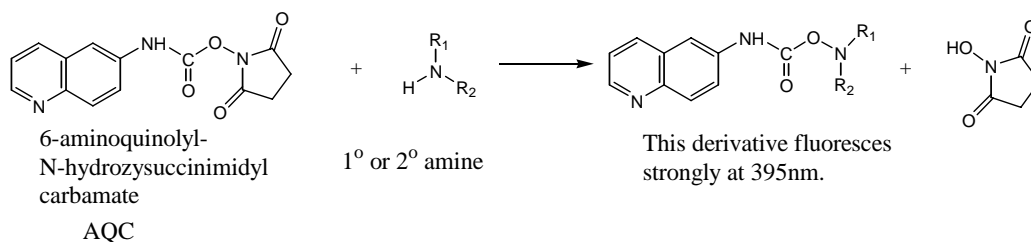


Figure 4-1. Derivatization reaction of –NH₂ containing compounds to form fluorescent derivatives

The detailed procedure for analyzing the –NH₂ containing compounds is given in Appendix 4-4. A brief description is given below. 500 µl of aerosol water extract is transferred to a derivatization tube and evaporated to dryness under a gentle stream of N₂. To the derivatization tube, 20 µl of internal standard and 160 µl of buffer are added. N₂ is bubbled into the mixture for 50 min to remove NH₃. Otherwise NH₃ peak would interfere the determination of Histamine and Arginine if an aerosol sample contains a large amount of NH₄⁺. Then 40 µl of the derivatization agent is added. The mixture is mixed with a vortex mixer for 1 min followed by heating at 55°C for 10 min. The sample is transferred to a 150 µl autosampler vial insert. Finally 10 µl is injected into a HPLC system for analysis. The hydrolysis step for analysis of the combined amino acids is as follows. 0.5ml of aerosol water extract and 0.5 ml of 12M HCl are mixed in a 3-ml all-Teflon vial. The vial is placed in an oven at 110°C for 24 hr. After cooling, 500 µl of the hydrolysate is transferred to a derivatization tube. The remaining procedure is the same as that for the free amino acids.

4.3.3 Carbohydrates

Carbohydrates merit consideration as components in ambient aerosols. As major constituents of organism, they are ubiquitous in the environment. Monomeric carbohydrates (monosaccharides and their derivatives) have high water solubility because of the multiple number of polar functional groups in each molecule. Each monosaccharide molecule contains 3 to 9 carbon atoms, all of which but one bear a hydroxy group. The remaining carbon atom is part of a carbonyl group. Monosaccharide derivatives comprise compounds derived from monosacchrides by reduction of the carbonyl group (i.e. sugar alcohols) or by oxidation of one or more terminal groups to carboxylic acids (i.e. sugar acids).

Total carbohydrate concentrations are measured based on the following measurement principle. The principle is to convert various monomeric carbohydrate forms into alditols, every molecule of which produces two molecules of formaldehyde upon periodate oxidation (Johnson and Sieburth, 1977). Formaldehyde is determined as its 2,4-dinitrophenyl hydrozone (DNPH) derivative using HPLC-photodiode array detection. Figure 4-2 illustrates the reaction sequences leading to the quantitative relationship between one molecule of carbohydrate (*e.g.* glucose) and the end product formaldehyde.

As carbohydrates in aerosol are determined after conversion to formaldehyde, any formaldehyde that might have been absorbed by the filter during sample collection and

storage would contribute to the formaldehyde concentration measured. When one computes the carbohydrate concentrations, it is necessary to correct for formaldehyde present in aerosol water extracts. The determination of formaldehyde in a water extract sample is also described in Appendix 4-5.

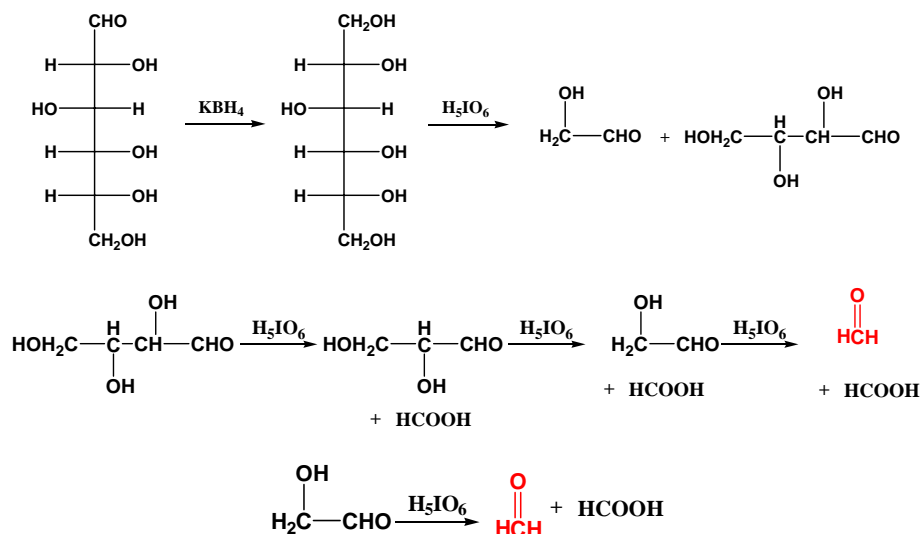


Figure 4-2. Reaction sequence of the formation of formaldehyde from a monomeric carbohydrate using glucose as an example

Both monomeric and polymeric carbohydrates could be present in the WSOC fraction of ambient aerosols. A hydrolysis step is necessary to break down polymeric carbohydrates into monomeric carbohydrates before the reaction scheme in Fig. 4-2 can be utilized to measure polymeric carbohydrates. The details for the analysis of carbohydrates are provided in Appendix 4-5.

Glucose and levoglucosan are used as model compounds for monomeric and polymeric carbohydrates for calibration, respectively. Levoglucosan is not a polymeric carbohydrate, but it breaks down to formaldehyde only after hydrolysis step, which behaves the same as polymeric carbohydrates. Levoglucosan is selected because its occurrence in aerosol is established.

4.3.4 Aromatic acids, hydroxy acids, oxo-carboxylic acids, and dicarbonyls

These three classes of compounds are analyzed in one injection using a two-step derivatization reaction scheme (Yu *et al.*, 1998). First, $-\text{C}=\text{O}$ groups are derivatized using O-(2,3,4,5,6-pentafluorobenzyl) hydroxy amine (PFBHA). Then $-\text{COOH}$ groups are derivatized using a silylation reagent, N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), to give trimethylsilyl (TMS) derivatives (Fig. 4-3). The resulting derivatives are easily resolved by a GC column. Their identification is assisted by their chemical ionization (CI) and electronic ionization (EI) mass spectra (Yu *et al.*, 1998). The detailed analysis procedure is provided in Appendix 4-6.

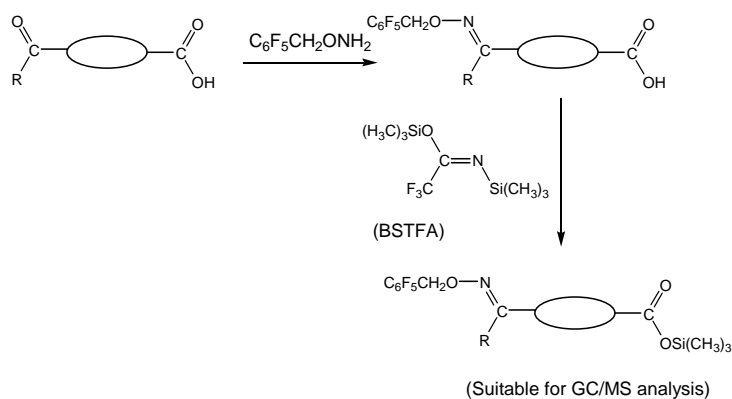


Figure 4-3. Derivatization reactions of oxo-acids and aromatic acids to form derivatives suitable for GC/MS analysis

5 Overall chemical composition

The relative aerosol mass distributions of the major constituents are plotted in Figure 5-1. Table 5-1 lists the concentrations of the major constituents, which include elemental carbon (EC), organic carbonaceous materials, sulfate, nitrate, chloride, ammonium, and other cations (sum of Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). The remaining mass, falling in the category of “others” in Figure 5-1, could include those of aerosol water, silicate, and metal species other than the soluble Na, K, Mg, and Ca. A conversion factor of 1.4 is used to calculate organic aerosol mass from organic carbon mass. All the concentration data are measurements derived from day-1+3 samples. The mass measurement was done by EPD; the EC and OC measurement was based on the thermal/optical transmittance method and carried out by the Government Laboratory. The other measurements were made by my group at HKUST.

A clear spatial difference is seen in the relative mass contributions of EC and OC. The two forms of carbonaceous materials account for 13-29% of the aerosol mass at the rural site Hok Tsui, 37-44% at Tsuen Wan, and 57-68% at Mong Kok. The organic carbonaceous materials account for 8-23%, 18-30%, and 27-38% of the aerosol mass at Hok Tsui, Tsuen Wan, and Mong Kok, respectively. At all three sites, the organics are an important fraction of aerosol mass, which demonstrates the importance of characterization of this fraction. Materials and discussions below focus on a sub-fraction of the organic carbon, the water-soluble organic carbon (WSOC) fraction.

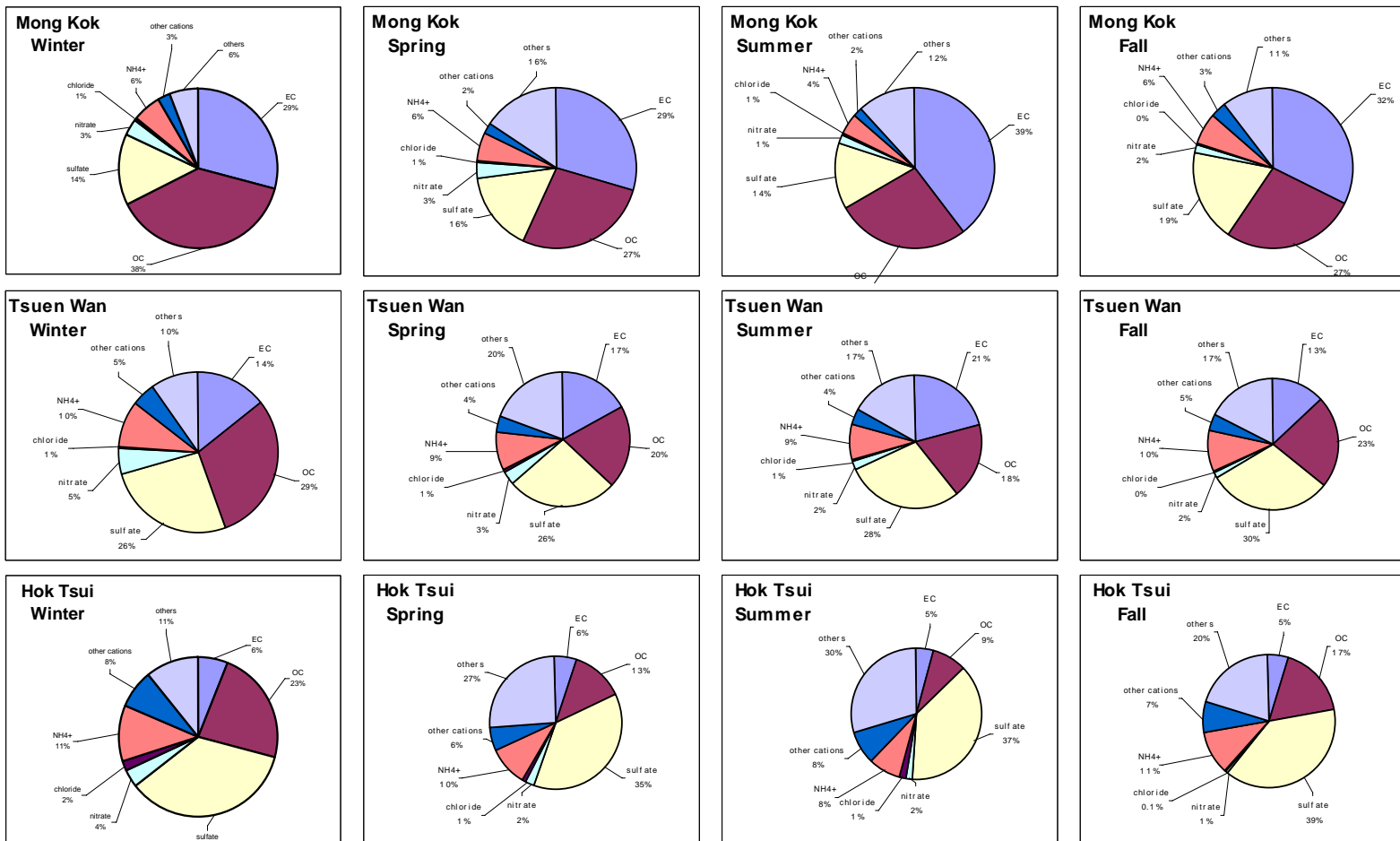


Figure 5-1. Relative aerosol mass distribution of the twelve seasonal composites among the major constituents.

Table 5-1. Concentrations of major constituents in the day-1+day-3 seasonal composites

	mass μg/m ³	1.4*OC μg/m ³	EC μg/m ³	sulfate μg/m ³	nitrate μg/m ³	chloride μg/m ³	NH ₄ ⁺ μg/m ³	Na ⁺ μg/m ³	K ⁺ μg/m ³	Mg ²⁺ μg/m ³	Ca ²⁺ μg/m ³	Σunidentified μg/m ³
Mong Kok												
winter	68.66	26.31	20.03	9.95	2.20	0.42	3.95	0.91	0.71	0.10	0.52	3.57
spring	57.75	18.59	17.10	9.33	1.72	0.29	3.46	0.79	0.29	0.09	0.52	5.58
summer	54.31	18.50	21.37	7.49	0.81	0.28	2.34	0.97	0.14	0.09	0.45	1.86
fall	59.81	18.58	19.38	11.14	0.96	0.16	3.78	0.69	0.69	0.10	0.47	3.86
Tsuen Wan												
winter	43.63	13.06	6.27	11.28	2.33	0.28	4.15	1.19	0.86	0.11	0.61	3.49
spring	33.14	8.63	5.71	8.74	1.14	0.17	3.13	0.62	0.29	0.08	0.45	4.19
summer	28.40	7.67	6.11	8.06	0.62	0.17	2.50	1.11	0.19	0.09	0.52	1.36
fall	37.50	9.82	5.04	11.33	0.64	0.04	3.77	0.51	0.70	0.09	0.36	5.22
Hok Tsui												
winter	30.11	6.93	1.85	10.62	1.14	0.57	3.37	1.63	0.75	0.17	0.71	2.37
spring	23.87	3.92	1.33	8.63	0.52	0.18	2.33	0.85	0.24	0.10	0.55	5.21
summer	15.82	2.56	0.72	5.99	0.26	0.22	1.27	1.12	0.14	0.10	0.57	2.87
fall	27.61	5.20	1.44	10.39	0.23	0.02	3.03	1.00	0.59	0.13	0.53	5.05

6 Total water-soluble organic carbon concentrations

The concentrations of WSOC and its contributions to the total organic carbon mass are listed in Table 6-1. The seasonal pattern of WSOC concentration is consistent among all three sites, i.e., winter > fall > spring > summer. This is in general agreement with the seasonal pattern of the aerosol mass loading (Table 5-1). The fraction of WSOC in OC also shows a consistent seasonal pattern for all sites, with the fall composites having the highest fraction and the other three seasonal composites having comparable values. WSOC accounts for a significant portion of the total organic carbon mass, ranging from 14% to 64%, with the highest WSOC contribution in the winter composite at the Hok Tsui site and the lowest WSOC contribution in the summer composite at the Mong Kok site. The WSOC fraction in OC also shows clear spatial variation. The rural site has the highest WSOC fraction whereas the urban site Mong Kok has the lowest WSOC fraction in any a given season. This may be explained by the relative contribution of primary and secondary organic aerosols at the three locations. At the Mong Kok site, the aerosol loadings are heavily influenced by the local vehicular emission sources and other primary emission sources (e.g. cooking fumes). The Hok Tsui site has no major local emission sources. The emission from marine vessels is likely minor. As a result, aerosols are mainly transported there from the neighboring urban centers. Secondary organic aerosols (SOA) are expected to have a larger contribution at the rural site. It is known that constituents of SOA are rich in polar functional groups such as hydroxyl, carbonyl, and carboxyl (Yu et al., 1999; Kalberer et al., 2000). The polar nature of the SOA constituents renders them more water-soluble. The OC/EC ratio also supports the hypothesis of a more prominent contribution of SOA at the rural site. Each aerosol source has a characteristic EC content. As an air parcel ages, aerosol in this air parcel contains more of OC due to formation of SOA (Turpin et al., 1991), consequently leading to a higher OC/EC value. The OC/EC ratios are listed in Table 6-1. It is clear that OC/EC ratios are higher at Hok Tsui than Tsuen Wan and Mong Kok in any seasons. Mong Kok has the lowest OC/EC ratios of all the three sites.

Contribution of WSOC to TC has been measured in a number of studies for aerosol samples in different parts of the world (Table 2-1). The WSOC/TC ratios at Hok Tsui and Tsuen Wan are in general agreement with those reported. However, Mong Kok has much lower WSOC/TC ratios (5-11%) in all four seasons. This does not come as a surprise in view of the heavy influence from local vehicular emission, as indicated by the higher EC concentrations at this site (Table 6-1). The seasonal average EC concentrations range from 17 to 20 $\mu\text{gC}/\text{m}^3$, approximately 10 and 3 times as high as those at Hok Tsui and Tsuen Wan.

The water-soluble substances (WSS) in ambient aerosols play an important role in visibility degradation. This fraction of aerosol mass influences the size of particles under different humidity due to their capability of absorbing water. The water-soluble inorganic substances (WSIS) mainly consist of sulfate, nitrate, chloride, ammonium, sodium, and potassium ions. The inorganic species are routinely measured and their role in visibility reduction is well characterized. On the other hand, the water-soluble organic substances (WSOS) have been rarely measured. The WSOC concentrations measured in current study allow us to compare the relative mass contribution of WSIS and WSOS to the total water-soluble aerosol mass.

Table 6-1. Water-soluble organic carbon concentrations and relative contributions to the total organic carbon mass and total water-soluble aerosol mass

	Aerosol mass $\mu\text{g}/\text{m}^3$	EC $\mu\text{gC}/\text{m}^3$	OC $\mu\text{gC}/\text{m}^3$	WSOC $\mu\text{gC}/\text{m}^3$	WSOC/OC	WSOC/TC	OC/EC	WSOS ^a $\mu\text{g}/\text{m}^3$	WSIS ^b $\mu\text{g}/\text{m}^3$	WSOS/WSS ^c
Mong Kok										
Winter	68.66	20.03	18.79	4.32	23%	11%	0.94	8.99	18.76	32%
spring	57.75	17.10	13.28	2.22	17%	7%	0.78	4.74	16.49	22%
Summer	54.31	21.37	13.21	1.88	14%	5%	0.62	4.02	12.59	24%
Fall	59.81	19.38	13.27	3.44	26%	11%	0.68	7.26	17.99	29%
Tsuen Wan										
Winter	43.63	6.27	9.33	3.81	41%	24%	1.49	8.00	20.82	28%
spring	33.14	5.71	6.17	1.83	30%	15%	1.08	3.95	14.62	21%
Summer	28.40	6.11	5.48	1.58	29%	14%	0.90	3.41	13.28	20%
Fall	37.50	5.04	7.02	3.17	45%	26%	1.39	6.71	17.42	28%
Hok Tsui										
Winter	30.11	1.85	4.95	3.15	64%	46%	2.67	6.61	18.98	26%
spring	23.87	1.33	2.80	1.36	49%	33%	2.10	3.02	13.40	18%
Summer	15.82	0.72	1.83	0.91	50%	36%	2.54	2.06	9.67	18%
Fall	27.61	1.44	3.72	2.19	59%	43%	2.59	4.77	15.92	23%

^a: WSOS denotes water-soluble organic substances.

^b: WSIS denotes water-soluble inorganic substances.

^c: WSS denotes water-soluble substances. WSS is the sum of WSOS and WSIS.

One needs to apply a conversion factor to obtain WSOS mass from WSOC to account for the non-carbon atoms (i.e., H, O, N) in aerosol constituents. The conversion factor apparently depends on the aerosol chemical composition, as a result, is specific to each location. The detailed chemical speciation allows us to calculate the conversion factors for each class of water-soluble organic compounds. For example, organic anions, free amino acids, combined amino acids, and aliphatic amines have a conversion factor of 3.3, 2.2, 2.7, and 2.5, respectively. The un-identified fraction of WSOC is assumed to have a conversion factor of 2. The WSOS mass is computed using the following equation,

$$m_{wsos} = \sum (mass_identified_fractions) + CF \times (WSOC - \sum (C_mass_identified_fractions))$$

where CF is the aerosol mass to carbon mass conversion factor for the un-identified portion in WSOC.

Table 6-1 lists the estimated WSOS and the measured WSIS mass concentrations. The WSIS concentrations are obtained by summing those of sulfate, nitrate, chloride, nitrite, NH_4^+ , K^+ , Na^+ , Mg^{2+} , and Ca^{2+} . The organic fraction accounts for a significant portion of the total water-soluble mass, ranging from 18-32%.

It is noted that carbonaceous materials in Mong Kok are 4-8 times as much as those in Hok Tsui whereas water-soluble organic and inorganic substances are similar in concentrations at all three sites (Table 6-1). The EC concentrations show even starker spatial difference. The EC levels at Mong Kok are approximately 10 times as high as those at Hok Tsui in the winter, spring, and fall, and 20 times as high in the summer. EC is exclusively produced in combustion processes. This again indicates that primary emissions contribute significantly to the aerosol loadings in Mong Kok. The contribution from secondary processes is more uniform over different parts of Hong Kong.

7 Speciation of the water-soluble organic fraction

Table 7-1 and Figure 7-1 summarize the concentrations of various WSOC species. All the species are expressed in the unit of ngC/m^3 to facilitate comparison of relative contribution to the water-soluble organic carbon mass. The identified WSOC species account for 12-29% of WSOC mass, leaving the majority of WSOC mass un-characterized.

Table 7-1. Concentrations of various WSOC components

	WSOC ugC/m ³	Σun-identified ngC/m ³	Σidentified ngC/m ³	MCH ^a ngC/m ³	Σorg ions ^a ngC/m ³	FAA ^a ngC/m ³	ali- amine ^a ngC/m ³	CAA ^a ngC/m ³	Combined ali-amine ngC/m ³	aromatic acids	hydroxy acids	oxo- acids	oxo- dicarbonyls	%identified (C mass)
Mong Kok														
winter	4.32	3819	499	78	165	48.7	6.2	58.8	4.1	101.5	24.6	8.3	2.8	12%
spring	2.22	1904	317	53	142	60.9	10.0	35.3	0.0	5.5	8.8	0.7	1.3	14%
summer	1.88	1589	292	66	126	47.6	5.1	23.0	1.3	10.6	9.2	1.8	0.8	16%
Fall	3.44	2900	539	114	184	82.3	9.1	89.4	3.7	36.3	14.8	2.5	2.4	16%
Tsuen Wan														
winter	3.81	3354	454	68	186	47.1	6.3	58.5	2.3	54.9	22.3	6.5	2.7	12%
spring	1.83	1550	285	42	145	61.4	6.7	16.0	0.0	5.0	7.2	0.3	0.9	16%
summer	1.58	1265	312	64	133	57.2	6.0	31.8	0.7	8.4	8.1	2.3	1.0	20%
Fall	3.17	2694	475	116	190	74.3	8.5	53.4	2.3	13.9	12.7	1.4	2.6	15%
Hok Tsui														
winter	3.15	2742	406	63	212	38.6	3.8	45.8	1.4	23.9	10.0	4.4	2.7	13%
spring	1.36	1035	328	50	152	40.3	3.8	66.6	1.2	5.1	6.4	0.4	2.8	24%
summer	0.91	651	261	65	126	38.7	2.6	21.2	1.5	0.4	3.5	0.9	1.6	29%
Fall	2.19	1773	421	87	212	60.2	6.6	34.1	0.0	2.9	13.0	0.4	4.3	19%

^a: MCH denotes monomeric carbohydrate-like compounds; org ions denote organic ions; FAA denotes free amino acids; Ali-amine denotes aliphatic amines; CAA denotes combined amino acids.

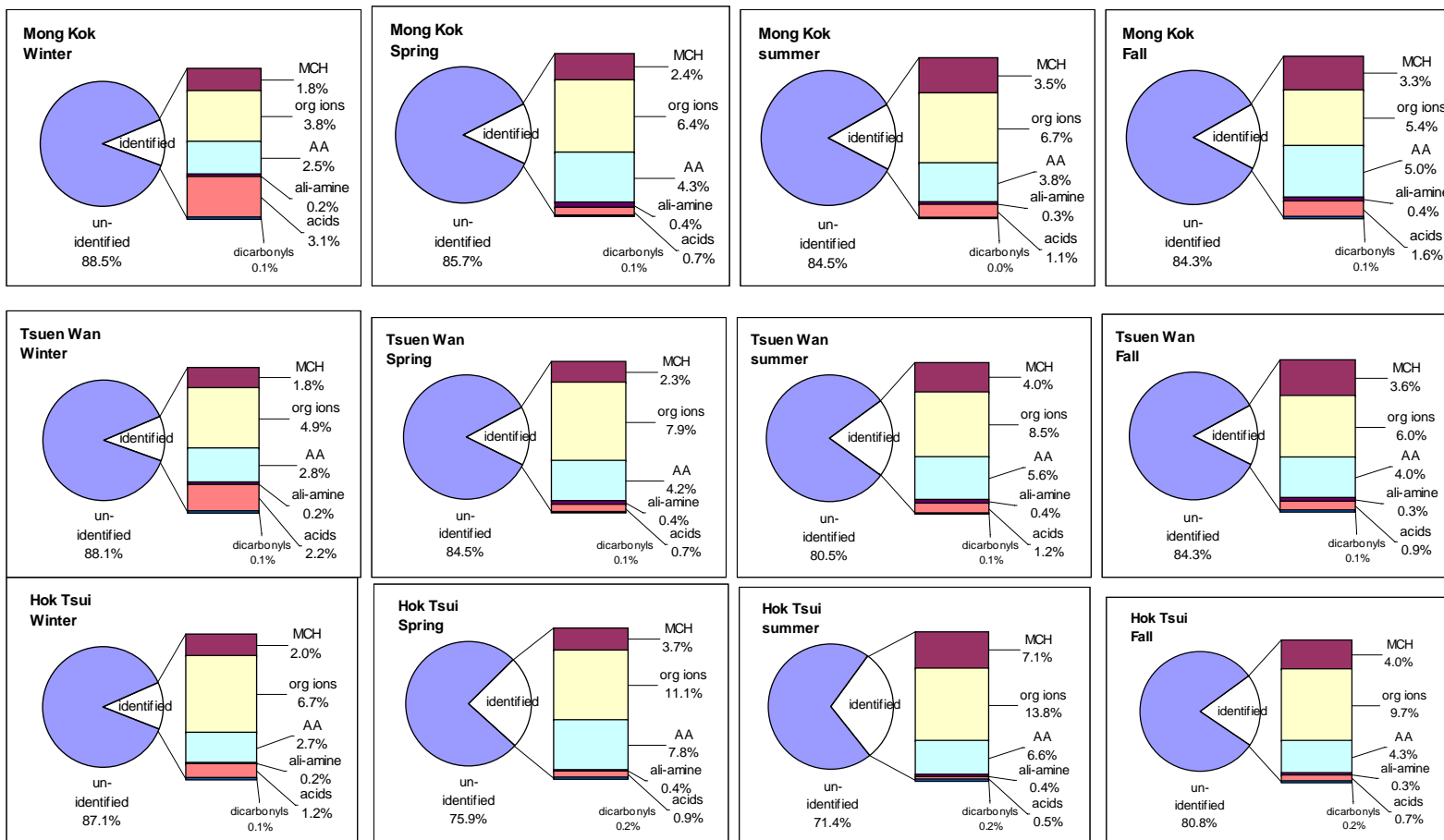


Figure 7-1. Relative WSOC mass distribution of the twelve seasonal composites.

(MCH denotes monomeric carbohydrates; org. ions refer to those species measured by IC; AA includes both free and combined amino acids; ali-amine refers to the sum of three aliphatic amine species in both free and combined forms; acids include aromatic acids, hydroxy acids, and oxy-acids; dicarbonyls include glyoxal and methylglyoxal.)

7.1 Organic anions, inorganic anions, and cations

Although the focus of our study is to characterize the organic compounds in the water-soluble aerosols, water-soluble inorganic anions and cations are also measured to compare the relative contribution of water-soluble inorganic and organic substances (see above).

A comparison is made between major inorganic ion measurements using day-2 and day-1 + day-3 samples (Figure 7-2). The major inorganic ions, i.e. sulfate, nitrate, and chloride, are measured for every individual day-2 filters. Their average seasonal concentrations are computed using the individual measurements. As shown in Figure 7-2, the nitrate and sulfate measurements are in good agreement, which adds to our confidence in the ion chromatographic measurements from both DRI and our lab. This also suggests that day-2 and day-1+3 result in equivalent seasonal average concentrations.

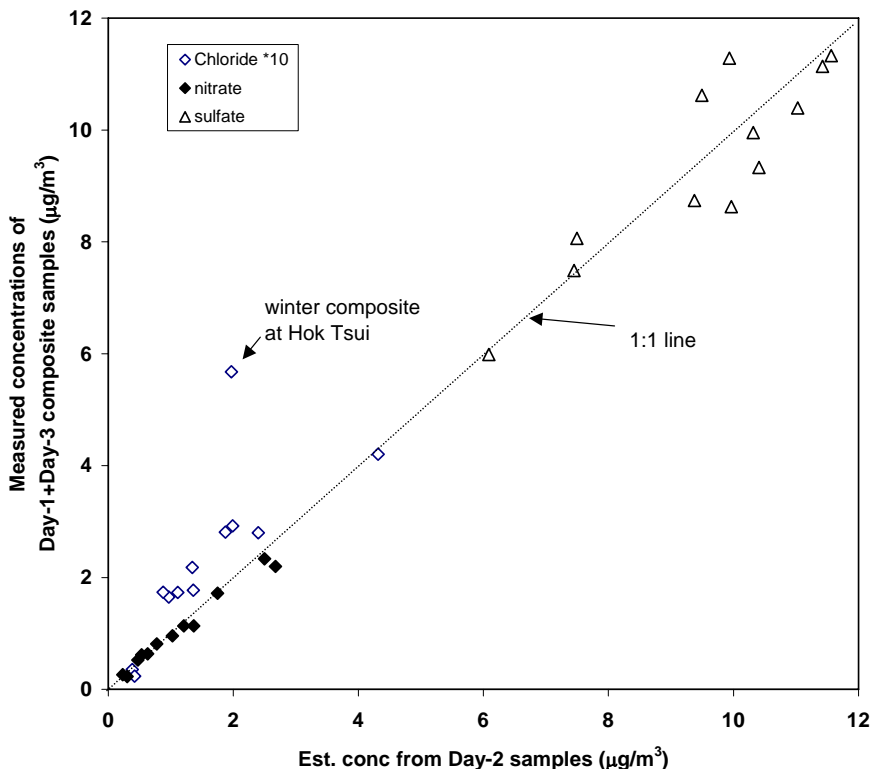


Figure 7-2. Comparison of major inorganic anion measurements using Day-2 and Day-1+Day-3 samples.

(Note that chloride concentrations are magnified by 10 times in the plot to facilitate easy visual comparison.)

Our chloride measurements using day-1+day-3 samples are generally higher than those derived from day-2 samples, and the Hok Tsui winter composite is noticeably much higher by our measurement. Chloride mainly comes from sea-salt. As a result, the majority of chloride resides in coarse particles and its concentration in PM 2.5 is much lower than those of nitrate and

sulfate. Our measurements show that the chloride concentrations are approximately 10 times lower than nitrate and 25 times lower than sulfate. An examination of chloride concentrations in day-2 samples reveals that many are below detection limit and have a zero concentration. On the other hand, our measurements are made on composites of 26-80 quarter-filters, which allows enough chloride for measurement. This difference may explain that the chloride measurements are higher than those derived from day-2 samples.

The same comparison is made for the cation measurements using day-2 and day-1+day-3 samples (Figure 7-3). The agreement for NH_4^+ and K^+ is reasonably good between the two sets of samples measured by the two labs. However, agreement is poor for Na^+ , with our measurements generally higher than DRI's measurements. It is noted that K^+ concentrations fall into two clusters. Winter and fall composites at the three sites form the high-concentration cluster ($0.59\text{-}0.86 \mu\text{g}/\text{m}^3$) whereas spring and summer form the low-concentration cluster ($0.14\text{-}0.29 \mu\text{g}/\text{m}^3$). K^+ is known to be emitted from biomass burning. The higher K^+ concentrations in the fall and winter composites may be related to the higher hill fire incidences during these two seasons.

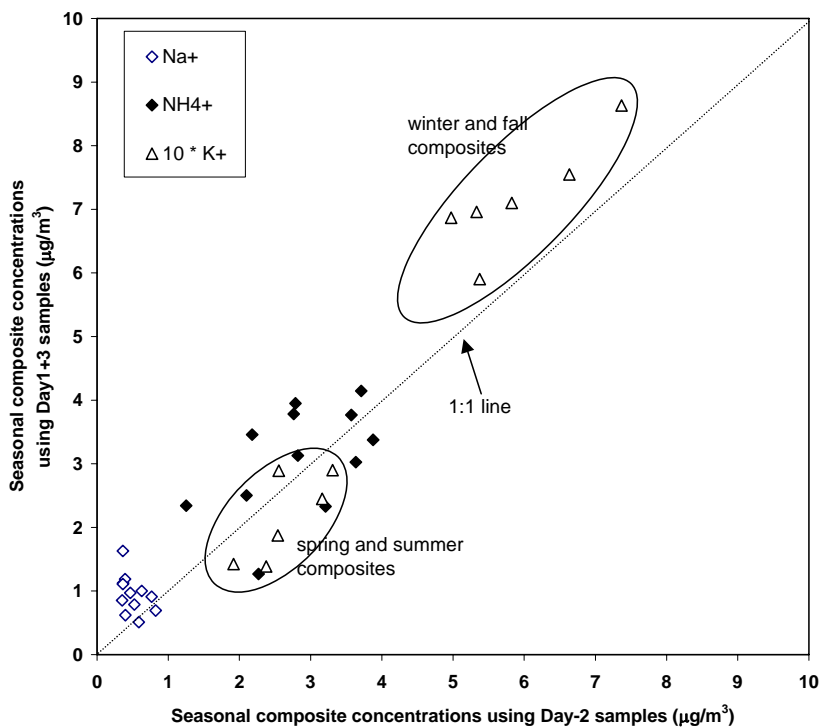


Figure 7-3. Comparison of cation measurements using Day-2 and Day-1+Day-3 samples.
 (Note that K^+ concentrations are magnified by 10 times in the plot to facilitate easy visual comparison.)

The concentrations of organic ions are summarized in Table 7-2. The detected species include methanesulfonic acid (MSA), pyruvate, oxalalic, malonic, maleic, succinic, and glutaric acids. Figure 7-4 shows a typical IC chromatogram for the anion species. The acidic species

could exist in the aerosols either as free acids or dissociate ions, and the relative distribution between the two forms depends on the aerosol acidity. The measurement method does not differentiate the two forms of these acidic species. Consequently, the concentrations reported here represent the sum of both forms for any given species.

Formate and acetate are also detected, but their concentration levels are indistinguishable from those in the field blank samples. Lactate and F⁻ co-elute under our IC analysis conditions. Our GC/MS analysis (described later) has confirmed the presence of lactate. Since it is not possible to differentiate lactate and F⁻ by IC, the quantification of lactate is based on GC/MS analysis. Pyruvate was also detected in some of the samples. Its free acid form, pyruvic acid, is among the species measured by GC/MS after derivatization. The GC/MS analysis provides better sensitivity than the IC measurement. As a result, quantification of pyruvic acid/pyruvate is based on the GC/MS analysis (see section 7.4).

Table 7-2. Concentrations of organic ions

	MSA ^a ng/m ³	oxalate ng/m ³	glutaric ng/m ³	succinic ng/m ³	malonic ng/m ³	maleic ng/m ³	Σorg ions ng/m ³	%WSOC (C mass)
Mong Kok								
Winter	33.4	482	0.0	15.1	52.3	72.2	655	3.8%
spring	23.2	392	38.8	13.2	37.3	27.4	532	6.4%
Summer	17.8	314	2.2	51.0	26.6	28.2	440	6.7%
Fall	11.1	515	43.0	89.2	25.3	28.2	712	5.4%
Tsuen Wan								
Winter	23.2	435	37.5	12.4	46.6	91.6	647	4.9%
spring	20.6	384	28.5	6.0	28.2	49.2	517	7.9%
Summer	18.6	334	2.2	46.2	38.7	27.8	468	8.5%
Fall	14.2	451	8.6	97.1	46.8	28.5	646	6.0%
Hok Tsui								
Winter	27.4	408	9.6	38.6	44.3	57.8	585	6.7%
spring	22.6	411	10.4	9.1	27.5	37.3	517	11.1%
Summer	17.9	318	2.2	25.9	55.0	27.8	447	13.8%
Fall	13.8	434	19.8	78.0	50.5	27.2	624	9.7%
Min	11.1	313.9	0.0	6.0	25.3	27.2	440	3.8%
Max	33.4	514.8	43.0	97.1	55.0	91.6	712	13.8%

^a: MSA denotes methylsulfonic acid.

Oxalic acid is found to be the most abundant dicarboxylic acid, accounting for 70-80% of the total dicarboxylic acid mass. Its concentration ranges from 0.3–0.5 μg/m³ at the three sites. There is no clear seasonal pattern. In addition, the concentrations levels are similar at all three sites. Pollutants that are mainly of primary origin and emitted throughout the year would exhibit low concentrations in the summer and higher concentrations in the winter due to the lower mixing height in the winter. Our observation of oxalic acid seasonal pattern is consistent with the observation for this compound in PM_{2.5} in California (Poore, 2000). Both the seasonal and spatial patterns suggest that the dominant source for oxalic acid is not from primary emission.

This in turn indicates that the major formation pathway for oxalic acid is secondary, e.g., atmospheric oxidation.

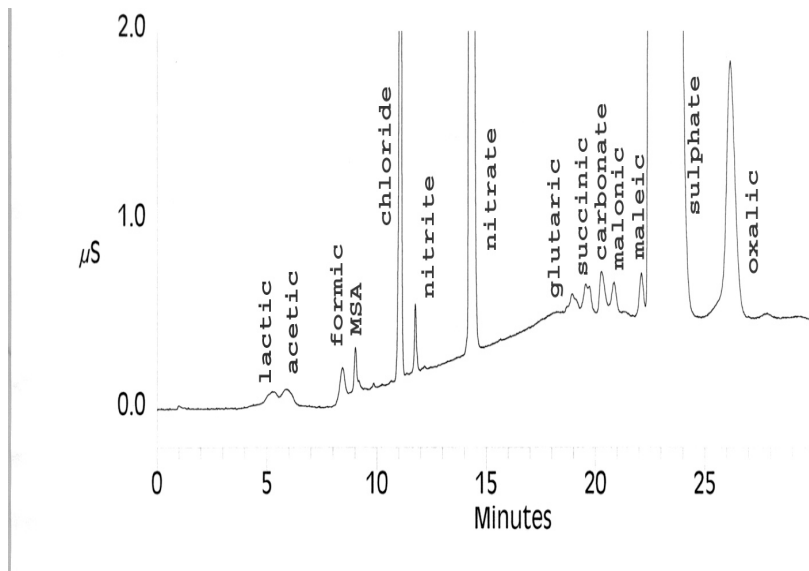


Figure 7-4. The anion IC chromatogram of the Mong Kok spring composite sample.

Other dicarboxylic acids (C₃-C₅) are much less abundant than oxalic acid. A good correlation ($r^2=0.81$, $n=11$) is found between oxalic acid and the sum of C₂-C₅ dicarboxylic acids (Figure 7-5). This suggests that C₂-C₅ dicarboxylic acids may have the same sources.

MSA ranges from 11 to 33 ng/m³, and its concentration levels are similar at all three sites. MSA is known to be an oxidation product of dimethyl sulfide (DMS), a biogenic sulfur species emitted from the oceans. All three sites show the same trend, i.e., MSA concentration being winter > spring > summer > fall. The similar concentration levels at all three sites are consistent with its oceanic origin and photooxidation production pathway.

The MSA concentration in air is determined by the relative strength of formation and removal processes. The production rate of MSA is controlled by many factors. The attack by OH on DMS is believed to be the first step (Yin et al., 1990). The concentration of OH radical is generally higher in polluted air masses than clean marine air masses. A portion of DMS (5-50%) is eventually oxidized to MSA (Saltzman et al., 1986). It has been observed that MSA is a more favorable oxidation product of DMS at lower temperatures (Berresheim, 1987). The lower temperatures and generally more polluted air in the winter favors the formation of MSA, however, the precursor DMS concentration is expected to be lower due to the less influence of marine air in the winter. The removal of MSA is controlled by wet and dry deposition (Hubert et al., 1996). The more frequent wet precipitation in summer certainly facilitates the removal of MSA. If we take all the affecting factors into consideration, it is possible that the concentration of MSA is higher in winter than in summer.

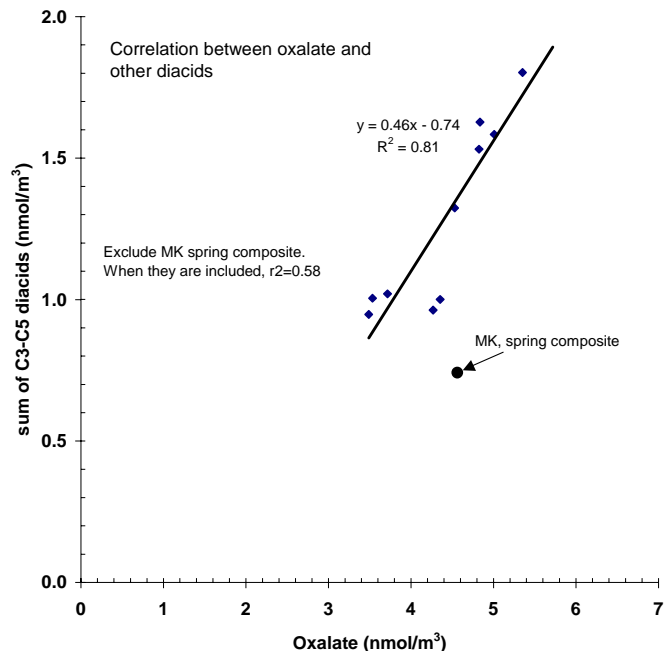


Figure 7-5. Correlation between oxalic acid and the other dicarboxylic acids.

7.2 Amino acids and aliphatic amines

Amino acids and aliphatic amines can exist either in free or combined form. We have measured both forms. The combined form is converted into the free form by hydrolysis, followed by analysis of the resulting hydrolysates for the free form. Table 7-3 summarizes the concentrations of amino acids and aliphatic amines in both combined and free forms.

The individual amino acids and aliphatic amines detected are listed in Figure 7-6. Among the AA species, glycine and valine are the two most abundant amino acids. The two amino acids alone account for 56-86% (by mole) of the total free amino acids. The next two most abundant free amino acids are alanine and β -alanine, accounting for 4-10% and 3-5% of the total free amino acids, respectively. An example of the relative composition of amino acids and aliphatic amines is given in Figure 7-7. The correlation between the major free amino acids is examined. Alanine and β -alanine are highly correlated ($r^2=0.75$, $n=12$) whereas the correlation between glycine and valine was marginal ($r^2=0.1$, $n=12$). Such various correlations may suggest that there are multiple sources of free amino acids.

Three aliphatic amines, methyl amine, ethyl amine, and ethanol amine, are identified to be present in every sample. Methyl amine is the most abundant aliphatic amine species.

It is noted that the levels of total amino acids and total aliphatic amines in either free form or combined form correlate well ($r^2=0.80$, $n=12$ for the free form; $r^2=0.78$, $n=12$ for the

free+combined form), suggesting that the two classes of compounds may come from the same source (Figures 7-8a and 7-8b). Amino acids, as building blocks of living species, are obviously of biological origin. They account for a small fraction of the WSOC mass, ranging from 2.5-7.8%. Aliphatic amines account for an even smaller fraction of the WSOC mass (0.2-0.4%). If one compares the relative concentrations of amino acids and aliphatic amines on a molar basis, the three aliphatic amines are about one-third of the abundance of the amino acids.

Table 7-3. Concentrations of amino acids and aliphatic amines

	FAA ^a ng/m ³	ali-amine ^a ng/m ³	CAA ^a ng/m ³	C-ali-amine ^a ng/m ³	%WSOC (C mass)	
					(F+C)AA ^a	Ali-amine
Mong Kok						
winter	113	14.9	157	10.4	2.5%	0.2%
spring	140	24.6	90	0.0	4.3%	0.4%
summer	105	12.4	64	3.2	3.8%	0.3%
fall	192	22.4	229	8.8	5.0%	0.4%
Tsuen Wan						
winter	114	15.3	152	6.0	2.8%	0.2%
spring	134	16.5	51	0.0	4.2%	0.4%
summer	123	14.8	87	1.7	5.6%	0.4%
fall	169	21.0	141	5.7	4.0%	0.3%
Hok Tsui						
winter	91.5	9.2	118	3.4	2.7%	0.2%
spring	92.7	9.4	163	2.8	7.8%	0.4%
summer	83.9	6.4	57	3.5	6.6%	0.4%
fall	144.3	16.6	93	1.8	4.3%	0.3%
min	83.9	6.4	50.7	0.0	2.5%	0.2%
max	191.8	24.6	228.6	10.4	7.8%	0.4%

^a: FAA denotes free amino acids; Ali-amine denotes aliphatic amines; CAA denotes combined amino acids; C-ali-amine denotes combined aliphatic amines; (F+C)AA denotes the sum of FAA and CAA.

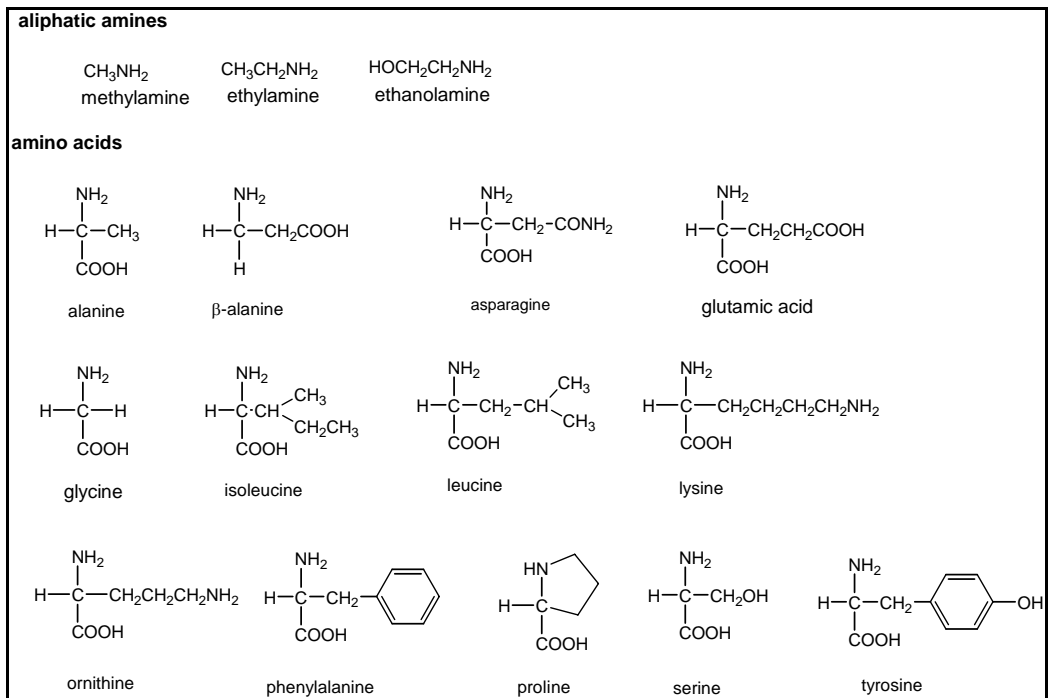


Figure 7-6. Chemical structures of amino acids and aliphatic amines detected in this study

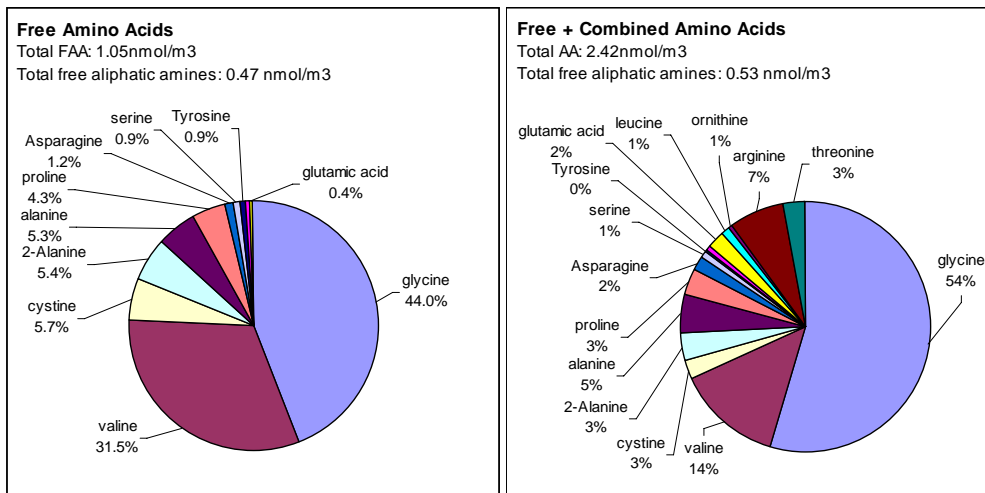


Figure 7-7. Relative composition of free amino acids and free + combined amino acids in the Hok Tsui fall composite sample.

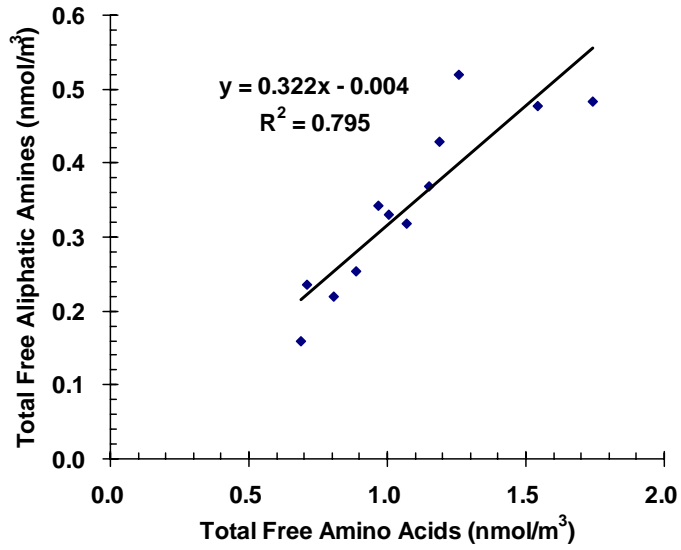


Figure 7-8a. Correlation between free amino acids and free aliphatic amines

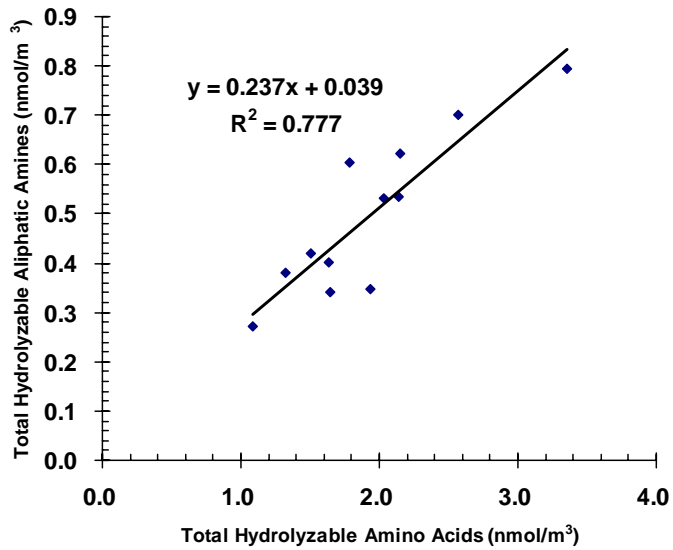


Figure 7-8b. Correlation between hydrolyzable (free+ combined) amino acids and aliphatic amines

7.3 Carbohydrate-like compounds

Table 7-4 summarizes the seasonal monomeric carbohydrate (MCH) concentrations at the three sites. The concentrations in ng/m³ are calculated from the values in nmol/m³, assuming the typical carbohydrate compound in the aerosols contain 6 carbon atoms, e.g., glucose. At this stage, only limited speciation work has been carried out for the carbohydrates. As a result, it is impossible to check the validity of the above assumption. The monomeric carbohydrates account for 1.8–7.1% of the WSOC mass if one assumes that typical MCH molecules are C₆ carbohydrates. No obvious seasonal or spatial pattern can be discerned.

Table 7-4. Concentrations of monomeric carbohydrates

	MCH ^a nmol/m ³	MCH ng/m ^{3b}	%WSOC (C mass)	glycerol nmol/m ³	ng/m ³	Glycerol/MCH by mole
Mong Kok						
winter	1.09	195	1.8%	0.005	0.6	0.4%
spring	0.74	133	2.4%	0.077	10.3	10.5%
summer	0.92	165	3.5%	0.047	6.2	5.1%
fall	1.58	285	3.3%	0.072	9.6	4.6%
Tsuen Wan						
winter	0.94	170	1.8%	bb ^c	bb	0.0%
spring	0.58	104	2.3%	0.079	5.4	13.7%
summer	0.88	159	4.0%	0.047	3.7	5.3%
fall	1.60	289	3.6%	0.085	3.9	5.3%
Hok Tsui						
winter	0.87	157	2.0%	0.051	7.1	5.8%
spring	0.69	125	3.7%	0.020	2.6	2.9%
summer	0.90	162	7.1%	0.034	4.5	3.8%
fall	1.21	218	4.0%	0.006	0.6	0.5%
min	0.58	104	1.8%	0.005	0.6	0.0%
max	1.60	289	7.1%	0.085	10.3	13.7%

^a: MCH denotes monomeric carbohydrates.

^b: The concentration in ng/m³ is calculated by assuming the typical MCH contain 6 carbon atoms, e.g., glucose.

^c: Below field blank.

The limited speciation work is based on the GC/MS analysis of the water extract residue after its silylation treatment by BSTFA. Glycerol is identified to be present in 11 out of the 12 composite samples. Table 7-4 lists the glycerol concentrations in the samples. The molar percentage contribution of glycerol to the total MCH ranges from 0 to 14%. It seems that all the winter composite samples have low or below blank levels of glycerol. At both Mong Kok and Tsuen Wan, the glycerol levels in the spring are higher than those in the other seasons. The reasons are not clear yet.

MCH compounds are not clear-cut to be of biological origin. For example, glycerol, a C₃ carbohydrate, is known to be emitted from cooking operations (Nolte et al., 1999) as a result of hydrolysis of cooking oil.

7.4 Aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls

The analysis scheme outlined in section 4.3.4 has positively identified the following nine compounds in four categories (see Figure 7-8 for their chemical structures).

- ✓ Aromatic acids: benzoic acid and phthalic acid
- ✓ Hydroxy acids: lactic acid, glycolic acid, and malic acid
- ✓ Oxo-acids: glyoxylic acid and pyruvic acid
- ✓ Dicarbonyls: glyoxal and methylglyoxal.

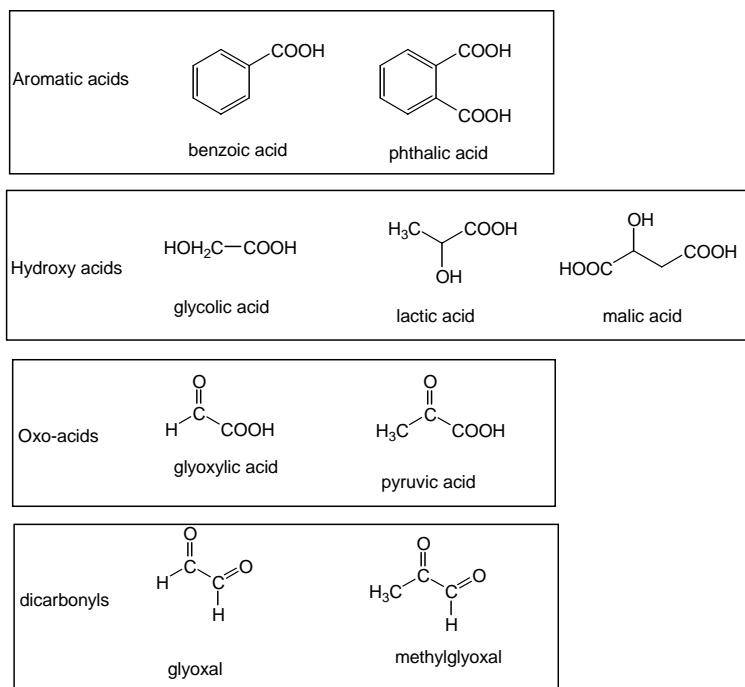


Figure 7-8. Chemical structure of aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls identified in the samples.

The concentrations of these chemicals are listed in Table 7-5. Phthalic acid concentrations range from non-detectable in the Hok Tsui summer composite to 175 ng/m³ in the Mong Kok winter composite. At all three sites, the winter composite has the highest concentration, followed by the fall composite. The summer and the spring composites have lower concentrations than the winter and the fall composites. Benzoic acid is detected in 4 out of the 12 composites, and its concentrations are much lower than phthalic acid. Benzoic acid is a relatively volatile compound. Most of benzoic acid is expected to reside in the gas phase. This may partially explain its low abundance in the aerosol phase. Both aromatic acids are likely produced from photooxidation of their corresponding aldehyde precursors, i.e. benzaldehyde and phthalaldehyde.

Table 7-5. Concentrations of aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls

	aromatic acids		hydroxy acids			oxo-acids		dicarbonyls		sum	%WSOC (C mass)
	benzoic	phthalic	glycolic	lactic	malic	glyoxylic	pyruvic	glyoxal	methylglyoxal		
Mong Kok	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	
winter	0.77	175	31.0	20.0	19.0	10.6	11.9	4.52	1.89	274	3.2%
spring	0.00	9.5	9.16	3.02	13.1	0.00	1.73	2.63	0.38	39.5	0.7%
summer	1.63	16.3	9.89	6.98	9.03	0.59	3.89	1.55	0.38	50.3	1.2%
fall	0.00	62.7	20.4	0.00	23.3	3.41	3.47	4.13	1.39	119	1.6%
Tsuen Wan											
winter	1.01	93.6	30.3	19.1	14.2	9.85	7.98	4.33	1.80	182	2.3%
spring	0.00	8.6	9.38	0.00	11.7	0.07	0.66	1.81	0.39	32.6	0.7%
summer	0.00	14.5	9.71	6.09	7.29	1.37	4.59	1.81	0.52	45.9	1.3%
fall	0.00	24.1	20.1	0.00	17.6	0.22	3.20	4.47	1.45	71.1	1.0%
Hok Tsui											
winter	0.00	41.3	14.7	5.22	9.20	6.97	5.18	3.74	2.35	88.7	1.3%
spring	4.65	3.2	8.03	0.00	10.9	0.00	0.90	3.93	2.27	33.9	1.1%
summer	0.52	0.0	5.09	0.00	5.31	0.00	2.18	2.24	1.28	16.6	0.7%
fall	0.00	5.1	19.9	0.00	18.7	1.35	0.00	5.95	3.63	54.6	0.9%
min	0.00	0.00	5.09	0.00	5.31	0.00	0.00	1.55	0.38	16.6	0.7%
max	4.65	175	31.04	20.0	23.3	10.57	11.9	5.95	3.63	274	3.2%

Two hydroxy acids, glycolic acid and malic acid, are positively identified in all of the composite samples. The third hydroxy acid, lactic acid, is detected in 6 out of the 12 composites. Their concentration ranges are 5-31, 0-20, and 5-23 ng/m³ for glycolic acid, lactic acid, and malic acid, respectively. The winter and the fall composites have higher concentrations of glycolic acid and malic acid than the spring and the summer composites. There is no discernible spatial variation, which suggests that they are unlikely associated with primary emissions.

The two oxo-acids, glyoxylic acid and pyruvic acid, exhibit similar seasonal and spatial characteristics to those of hydroxy acids. By the same logic, they are most likely of secondary origin. Their concentrations range from not detectable to 11 and 12 ng/m³ for glyoxylic and pyruvic acid, respectively.

The two dicarbonyls, glyoxal and methylglyoxal, again show similar seasonal and spatial characteristics to those of hydroxy acids and oxo-acids. They are known to have both primary emission sources (e.g. combustion) and secondary sources. Many volatile organic compounds, such as benzene, toluene, trimethylbenzenes, and isoprene, produce glyoxal and methylglyoxal upon degradation by atmospheric oxidants. The lack of spatial variation seems to suggest that secondary sources play a dominant role in their atmospheric abundance. There is a good linear correlation between the two dicarbonyls ($r^2=0.77$, $n=12$), indicating the factors affecting their formation rate are similar.

8 Summary

- Carbonaceous aerosols make up 53-73% of the aerosol loading at the Mong Kok site. The contribution of carbonaceous aerosol at Tsuen Wan and Hok Tsui is lower, but still account for a significant fraction (36-52% and 16-39%, respectively) of the aerosol mass. The OC/EC ratio is generally lowest in Mong Kok, followed by that in Tsuen Wan, and the highest in Hok Tsui. This indicates that carbonaceous aerosol loading is heavily influenced by primary emission (e.g. vehicular source) at Mong Kok whereas the secondary organic aerosol contribution becomes increasingly important at Tsuen Wan and Hok Tsui.
- The water-soluble organic carbon (WSOC) accounts for a significant portion of the total organic carbon mass, ranging from 14% to 64%. The highest WSOC contribution occurs in the fall composite at Hok Tsui, and the lowest in the summer composite at Mong Kok.
- Contrary to the stark spatial difference in the total carbonaceous mass, the water-soluble portion of organic aerosols is comparable in its concentration levels and shows much reduced spatial variation. The same spatial trend is observed for the secondary inorganic aerosols (i.e., sulfate and nitrate). This is consistent with spatial characteristics of secondary aerosols.
- The water-soluble aerosol constituents are especially important in aerosol's role in visibility reduction. Our measurements have shown that the water-soluble organic compounds account for a significant portion of the total water-soluble aerosol mass.

- The detailed chemical speciation work carried out so far has identified 12-29% of WSOC mass as organic anions, amino acids and aliphatic amines in free and combined form, carbohydrates, aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls.
- The organic anions detected by IC include methanesulfonic, pyruvate, and C₂-C₅ dicarboxylic acids. They account for 4-14% of the WSOC mass. Methanesulfonic acid has an oceanic origin. Oxalic acid is the most abundant organic acid species. It is found that the concentrations of other dicarboxylic acids correlate with those of oxalic acids, suggesting a common formation pathway. The lack of spatial variation in their concentrations also suggests that secondary formation pathways are dominant sources.
- Amino acids are of biological origin. They account for 3-8% of the WSOC mass. The most abundant amino acids are glycine and valine. Three aliphatic amines, methylamine, ethylamine, and ethanolamine, are also present in all the samples. The aliphatic amines account for 0.3-0.6% of the WSOC mass. Their concentrations are found to correlate with those of amino acids, indicating that aliphatic amines likely originate from the same biological sources.
- The total monomeric carbohydrates are determined and their carbon mass contribution to WSOC is estimated to be 2-7%. One carbohydrate species, glycerol, is positively identified and quantified in the samples. Glycerol contributes to 0-14% of the total monomeric carbohydrates.
- Two aromatic acids, three hydroxy acids, two oxo-acids, and two dicarbonyls are identified in the aerosol samples. The nine compounds summing up together account for 0.7-3.2% of the water-soluble organic carbon mass. No discernible spatial variation is observed for these compounds, suggesting that they are most likely of secondary origin

9 References

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