

**Twelve-month Particulate Matter Study
in Hong Kong**

Final Report

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ACRONYM

Aliphatic Hydrocarbon (AH)
Alkanols (ROHs)
Aluminum (Al)
Ammonium (NH_4^+)
Calcium (Ca)
Carbon Preference Index (CPI)
Carbon Number Maximum (C_{max})
Chemical Mass Balance 7 model (CBM 7 model)
Chloride ion (Cl^-)
Copper (Cu)
2,4-dinitrophenylhydrazine (DNPH)
Desert Research Institute (DRI)
Elemental Carbon (EC)
Energy Dispersive X-ray Fluorescence (EDXRF)
Fatty Acids/Alkanoic Acids (FAs)
Federal Reference Monitor (FRM)
Flame Ionization Detection (FID)
Gas Chromatography (GC)
Gas Chromatography/Mass Spectrometry (GC/MS)
Government Laboratory (GL)
High Performance Liquid Chromatography/ Ultra Violet Detection (HPLC/UV)
High Performance Liquid Chromatography (HPLC)
Hok Tsui (HT)
Hong Kong Observatory (HKO)
Hong Kong Environmental Protection Department (HKEPD or EPD)
Hong Kong University of Science and Technology (HKUST)
Interagency Monitoring of Protected Visual Environments (IMPROVE)
Iron (Fe)
Lead (Pb)
Manganese (Mn)
Mong Kok (MK)
National Research Council (NRC)
Nickel (Ni)
Nitrate ion (NO_3^-)
Organic Carbon (OC)
Organic Marker Compounds (OMC)
Polychlorinated Biphenyls (PCBs)
Polychlorinated Dibenzodioxins / Polychlorinated Dibenzofurans (PCDDs/PCDFs)
Polynuclear Aromatic Hydrocarbons (PAHs)
Potassium ion (K^+)
Particulate Matter (PM)
Quality Assurance/Quality Control (QA/QC)
Ratios of Unresolved Complex Mixture : Resolved n-alkanes (U:R)
Sea-level Pressure (SLP)

Silicon (Si)
Solvent Extractable Organic Compounds (SEOC)
Sodium ion (Na^+)
Speciation Trends Network (STN)
Standard Operating Procedure (SOP)
Sulfate ion (SO_4^-)
Tap Mun (TM)
Toxic Air Pollutants (TAP)
Tsuen Wan (TW)
Tapered Element Oscillating Micro Balance (TEOM)
Thermal Optical Reflectance (TOR)
Thermal Optical Transmittance (TOT)
Total Carbon (TC)
Unresolved Complex Mixture (UCM)
Uranium (U)
United States Environmental Protection Agency (USEPA)
Volatile Organic Compounds (VOC)
Water Soluble Organic Compounds (WSOC)
World Meteorological Organization (WMO)
Zinc (Zn)

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DISCLAIMER

Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

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EXECUTIVE SUMMARY

A 12-month study of PM_{2.5} mass concentration levels at strategic locations in Hong Kong to represent urban, roadside and rural environment in Hong Kong was conducted from November 2000 to October 2001. The main focus of the study is on chemical speciation of PM_{2.5} particulate with special focus on organic speciation: solvent extractable organic compounds; water soluble organic compounds, and organic tracer marker compounds. Additional supporting measurement on Toxic Air Pollutants during the 12-month PM_{2.5} chemical speciation project was also performed. The following is a summary of findings derived from the 12-month PM_{2.5} study in Hong Kong.

Meteorological Factors

- Hong Kong is situated in the sub-tropics along the southeast coast of China. The seasonal evolution of weather in Hong Kong is closely under the influence of the East Asian Monsoon system. Because of the intense heating effect of the Tibetan Plateau, the Asian monsoon system is the strongest and one of the most important components in the global circulation. Under the influence of the Asian monsoon, we typically have longer summers and winters and relatively shorter springs and falls in Hong Kong. These meteorological factors also play a significant role in chemical composition and pollutant levels in Hong Kong

PM_{2.5} Mass Concentration and Chemical Speciation

- A total of 1080 filters were sampled for the present project, close to 99% of the sampled filters are valid for gravimetric and analytical determination.
- PM_{2.5} fine particulate matters were collected on 47mm filters at a rural (Hok Tsui [HT]), an urban (Tsuen Wan [TW]) and a roadside (Mongkok [MK]) monitoring station in Hong Kong respectively during the period of November 2000 to October 2001. The filters were divided into four seasonal batches according to the observed variations of sea-level pressure and upper-level wind direction over Hong Kong.
- The annual averages of PM_{2.5} concentrations at TW, MK, and HT were found to be 34, 58, and 24 µg/m³ respectively in the 12 months study period. Mean mass concentrations of PM_{2.5} at TW, MK, and HT for four seasons in Hong Kong were found to be in the range of 26 - 44, 51 - 69, and 15 - 32 µg/m³. In terms of mass concentration levels, one overall observation can be made: Mong Kok>Tsuen Wan>Hok Tsui; roadside>urban>rural.
- Ammonium sulfate, organics, and soot (elemental carbon) are the most abundant species found at all the sites. The annual mean concentration of ammonia sulfate, organics, and soot are in the range of 11.9 to 12.7, 5.9 to 22.2, and 1.7 to 19.3 µg/m³ at MK, TW and HT respectively. At all sites, the geological material was found to represent only a small fraction of the total mass, ranging from only 0.6 to 2.2 µg/m³ or about 3% to 8% of the measured mass for the four seasons.

Solvent Extractable Organic Compounds

The results of a 12-month study of the seasonal and spatial variation of the solvent extractable organic compounds (SEOC) in fine suspended particulate matters in Hong Kong are incorporated in this report.

- The composite samples grouped by season were characterized and quantified for their concentrations of four classes of SEOC *viz* aliphatic hydrocarbons (AHs), polynuclear aromatic hydrocarbons (PAHs), fatty acids/alkanoic acids (FAs) and alkanols (ROHs) comprising over 100 individual compounds using gas chromatography-mass spectrometry. The weight of extractable organic compounds accounts for about 18 % and 8 % of the organic carbon (OC) for the roadside site and the rural site respectively.
- The total yield of SEOC and yields of resolved AHs, unresolved complex mixture (UCM), PAHs, FAs and ROHs were found to be in the ranges of 125-2060, 54.0-1510, 0.6-17.2, 41.6-520 and < 0.1-12.1 ng m⁻³ respectively. Distinct seasonal variations in the concentrations of the total and the four classes of SEOC are observed with higher concentrations in the winter samples and lower concentrations in the summer samples. This observation is in line with the previous findings on the concentrations of other semi-volatile organic pollutants and persistent organic pollutants in the atmosphere of Hong Kong (Louie and Sin 2002). Spatial variations are also very obvious with samples collected at the roadside station having the highest concentrations of SEOC in all seasons and the rural samples having the lowest concentrations.
- Characteristic ratios of petroleum hydrocarbons such as carbon preference index (CPI) and ratios between unresolved complex mixture and n-alkanes (U:R) were worked out for assignment of possible sources of fine suspended particulate matters. The findings suggest fine particulate matters in Hong Kong originate from both biogenic sources such as microbial activities and vascular plant wax and anthropogenic sources including vehicular exhaust and kitchen emission. Anthropogenic sources are estimated to contribute to about 93 % and 77 % of the fine particulate matters at the roadside and urban site respectively. This is the first report of its kind on which the SEOC profiles at typical urban and roadside locations where the city and street dwellers of Hong Kong are exposed to are reported.

Water-soluble Organic Compounds (WSOC)

Chemical characterization of the water-soluble organic compounds (WSOC) was performed as part of the 12-month PM_{2.5} study. 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 regarding the WSOC part of the

investigation are summarized below.

- The 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. Measurements conducted in the present study 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 mass from water-soluble organic compounds. 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 mass from water-soluble organic compounds. 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 mass from water-soluble organic compounds. No discernible spatial variation is observed for these compounds, suggesting that they are most likely of secondary origin.

Organic Tracer Marker Compounds

Data interpretation and write-up still in progress at time of issue of this report.

INTRODUCTION

1.1 About this Report

This report can be divided into two parts. A major part of this report focuses on gravimetric concentrations and chemical speciation of PM_{2.5} in Hong Kong, while a small part of this report deals with gaseous toxic air pollutants monitoring performed in the same monitoring period. The major part incorporates the second part as a needed complement that includes gaseous as well as particle components of toxic air pollutants. For ease of reference, Toxic Air Pollutants (TAP) sampling methods and sampling sites information are included in the 'Experimental' section of this report. In addition to tables and figures for documentation and illustration purposes, supporting information and reports are given in the Appendix Section of this report. All together, there are 10 appendices (Appendices 1 to 10) incorporated in this report.

1.2 Study Objectives

This is the first attempt that a comprehensive year-long PM_{2.5} aerosol characterization study in Hong Kong was launched. The study objectives aim to be practical, realistic, and achievable within the proposed timeframe and resources and these study objectives are:

- Evaluate sampling and measurement methods for inorganic and organic particulate components and for gases that are precursors and end-products of particle-forming atmospheric reactions.
- Determine the organic and inorganic composition of PM_{2.5} and how it differs by season and proximity to different source types.
- Based on ambient concentrations of marker compounds, source measurements performed elsewhere, and available Hong Kong emissions inventories, determine which sources are the most probable contributors to PM_{2.5} in Hong Kong.

1.3 Overview with Background Information about the 12-month Particulate Matter Speciation Project

A 6-month study on PM_{2.5} was conducted in 1998/99 and provided the EPD with preliminary information on fine particle situation in Hong Kong. This study identified that there is a strong association between carbon and fine particles rather than coarse particles. We also found that winter month organic carbon (OC) concentrations (14.0 µg/m³, Dec., 98) was more than double of summer month value (6.6 µg/m³, Aug., 98) [see also Table 1a and Appendix 1 for further information].

With carbonaceous species being one of the major components of the particulate matter, speciation information of organic carbon would be relevant for the understanding of air quality issues in Hong Kong. To this end, a 12-month PM_{2.5} study with special focus on chemical speciation was conducted from November 2000 to October 2002 in order to gain a better insight into the chemical composition of fine particulate matter of Hong Kong in different seasons. As chemical speciation is the prime objective of the present study, the sampled PM_{2.5} filters were subjected to an extensive array of chemical analysis methods. PM_{2.5} mass, elements, ions, organic carbon, elemental carbon, solvent extractable organic compounds (SEOC), water-soluble organic compounds (WSOC), and organic tracer markers. Where appropriate, continuous PM_{2.5} information as determined by the TEOM method and other gaseous parameters from the EPD ambient air monitoring network are incorporated into this report to facilitate a better understanding of fine particulate (PM_{2.5}) chemical composition in Hong Kong.

1.4 Background Information

High particulate levels are typically found in urban and roadside locations in Hong Kong (Pang, 1998, Lam, 1999). There are also growing evidences 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 identify toxicological constituents, sources, and long range transport issues (Cass, 1998, Chow and Egami, 1997, Poor, 2002, Zielinska, 1994, Fang et al, 1999). In addition, the chemical composition provides hints on the origins of the fine particulates, since certain compounds are of specific sources (Cass, 1988, Rogge et al, 1993, Schauer, 1996, Schauer, 1998). To formulate effective control strategies, policy-makers need to have knowledge of relative contribution from various PM_{2.5} sources.

Although a comprehensive literature review is beyond the scope of the present study, a comprehensive list of papers pertaining to Hong Kong's air pollution and particulate issues published is included to acknowledge the body of information that is currently available. Systematic evaluation and review of current measurement data and published materials may contribute towards the development of a conceptual model of the relationships between emissions, meteorology, and ambient concentrations in future work. These published papers are contributed from the following authors: Carras et al., 2002, Chan et al., 2001, Chan et al., 2002, Chan et al., 2002, Chan et al., 1998a, Chan et al., 1998b, Chan et al., 1999, Chan and Kwok, 2000, Chan and Liu, 2001, Chan et al., 2001a, Chan et al., 2001b, Chan and Kwok, 2001, Chan et al., 2002a, Chan et al., 2002b, Chan et al 2002c, Chang and Koo, 1986, Chao and Wong, 2002, Cheng and Lam, 1998, Cheng and Lam, 1999, Cheng et al., 2000, Choi and Chan, 2002, Chung et al., 1999, Duzgoren-Aydin et al., 2002, Fang et al., 1999, Fu et al., 1997, Fung et al., 2002, Hills, 1991, Ho and Lee, 2002, Ho et al., 2002, Ho, 1990, Hong et al., 1999, Kok et al., 1997, Koo et al., 1986, Lai and

Sequeira, 2001, Lam et al., 2001, Lau and Luk, 2001, Lau and Koenig, 2001, Lee et al., 1999a, 1999b, Lee, 2000, Lee and Chang, 2000, Lee et al., 2001a, Lee et al., 2001b, Lee et al., 2002a, Lee et al., 2002b, Lee et al., 2002c, Lee and Sequeira, 2002, Li et al., 2001, Lind and Kok, 1999, Liu et al., 2001, Liu and Chan, 2002, Lo and Yip, 1999, Luk, 1999, Malpas et al., 2001, Man and Shih, 2001, Manoj et al., 2000, Pang et al., 1998, Park and Kim, 1999, Peng et al., 2000, Physick and Goudey, 2001, Qin et al., 1997, Ruse and Peart, 2000, Sequeira and Lai, 1998, Sin et al., 2001, Tanner, 1999, Thornton et al., 1997, Tong et al., 1999, Tong and Lam, 2000, Wang et al., 1997, Wang et al., 2001, Wang et al., 2002, Wei, 1999, Wu and Chan, 2001, Yao et al., 2002, Yu, 1995, Yu, 2001, Yu et al., 2001, Yu et al., 2002, Zhang et al., 2001, Zheng et al., 1997, Zheng et al., 2000, Zheng and Fang, 2000, Zhuang et al., 1999.

Currently Hong Kong is facing two air pollution problems: One is the street level pollution mainly caused by the large number of motor vehicles, especially diesel vehicles, on Hong Kong streets; another air pollution problem that Hong Kong is facing is regional air quality pollution (Study of Air Quality in the Pearl River Delta Region 2002). The regional air quality problem is characterized by a gradual deterioration in visibility degradation and occasional episodes of high PM₁₀ levels and ozone pollution.

Table 1b summarized four major pollutant source categories namely energy (e.g. power generation), industry (e.g. cement production and printing), transportation (e.g. diesel exhaust and gasoline exhaust) and volatile organic compounds (VOC) containing product (e.g. domestic product and paint). This information should provide a better perspective on the possible urban source contributors in Hong Kong and Pearl River Delta Economic Zone (PRDEZ). Using VOC, PM₁₀, oxides of nitrogen (NO_x), and sulphur dioxide (SO₂) emission data as indicators, emissions from the four major sectors contributed at least 90% of the regional emission and the regional emissions for all the concerned pollutants are dominated by PRDEZ (Study of Air Quality in the Pearl River Delta Region 2002).

Elevated OC concentrations with strong association with fine fraction of particulate were also found in winter-time urban environment in Hong Kong (Leung, 1999). Based on organic carbon speciation data obtained in our TAP monitoring sites and information found in the literature, the organic compounds such as polycyclic aromatic compounds [PAHs] and other organic species are likely to be found. In a recent study reported by Zheng (Zheng, 1997, Zheng, 2000, Zheng and Fang, 2000), fatty acids and alkanols were included in addition to n-alkanes and PAHs to characterize the organic compounds in PM_{2.5} aerosols in Hong Kong. The predominated sources of organic pollutants may originate from incomplete combustion of fossil fuels especially from vehicle emissions, and biogenic sources.

In general, a diverse range of organic compounds can be found in the solvent extractable organic compounds (SEOC) adsorbed on the particulate matter. Although a large number of these compounds have been identified and quantified as n-alkanes and polycyclic aromatic compounds, unfortunately previous available

quantitative speciation information represent only a small fraction of the SEOC (Fu, 1997). With the inclusion of fatty acids and alkanols for the characterization of organic compounds in PM_{2.5} aerosols, a clearer picture is now emerging (Zheng, 1997, Zheng 2000).

To have a better understanding of these organic species, we can initially gauge the distribution of the organic carbon (OC) and elemental carbon (EC) species in both the fine (PM_{2.5}) and coarse fraction (PM₁₀ -PM_{2.5}) from data obtained from a previous 6-month study (Leung, 1999) conducted by EPD. While sampling and gravimetric determination were performed by EPD, analytical support of this preliminary study was performed by the Desert Research Institute (DRI). By way of subtracting the OC and EC values associated with fine fraction from PM₁₀, we can determine mathematically the OC and EC values in the coarse fraction. For comparison purpose, the OC and EC values in fine, coarse, and RSP fractions from the six-month study are presented in Table 1a.

While the OC and EC concentrations distributed in the fine fraction were in the ranges of 6.6 µg/m³ to 13.4 µg/m³, and 6.2 µg/m³ to 9.2 µg/m³, respectively, OC and EC concentrations in the coarse fraction ranges from 1.3 µg/m³ to 3.9 µg/m³, and 0.1 µg/m³ to 1.6 µg/m³. Apparently, there is a strong association between carbon (OC + EC) with the fine fraction rather than the coarse fraction. The increase in OC values from Aug 98 to Jan 99 is significant, especially in winter months. VOC monitoring data from Tsuen Wan and Central & Western sites in Hong Kong revealed that the ambient concentrations of BTEX (benzene, toluene, ethylbenzene and xylenes) were comparable to other urban cities and significant seasonal variation was found. Also, BTEX concentrations tended to peak in the relatively dry winter months in Hong Kong (Sin et al 2000). Obviously, it would be more direct and prudent to obtain the speciation information directly from the PM_{2.5} and PM₁₀ particulates collected for OC/EC determination. Nevertheless, the independent VOCs and PAHs data may serve the purpose of filling in the preliminary data gaps of OC found in PM_{2.5} and PM₁₀. Therefore, both VOCs and PAHs in ambient air data are included here for a more complete evaluation. However, we should bear in mind that a significant amount of VOCs were purged during the sampling process of particulate matters (Zielinska and Fujita, 1994).

1.5 Current Status of Characterization of Organic Compounds in Fine Particulates

1.5.1 Solvent extractable organic compounds

Carbonaceous materials (organic carbon (OC) and elemental carbon (EC)), could take up 20-80% of fine particulate mass (Jacobson, 2000). Most often chemical speciation of 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 compounds mass typically accounts for only 50-60% of the total organic aerosol (Cass, 1998). Rogge (Rogge,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 (Rogge, 1993), the UCM and all the identified resolved peaks account for 49% of all the aerosol OC mass, leaving the remaining 51% un-characterized.

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 Hong Kong University of Science and Technology (HKUST) campus. The sum of the measured species ranges from 56 to 234 ng/m³.

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 compounds mass remains unidentified. However, the percentage of organic solvent extractable compounds mass remains unidentified is included as part of the investigation in the solvent extractable organic compounds study in present project.

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 pg/m³ with 1-nitropyrene as the most abundant nitro-PAH. The study indicates that nitro-PAHs are minor components in PM_{2.5} aerosols in Hong Kong.

Compared with organic compounds speciation studies of PM_{2.5} aerosols, more studies have focused on the organic compounds 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, 1982). Values >2 reflect significant contribution from petroleum products (Simoneit, 1986).

1.5.2 Water-soluble organic compounds (WSOC)

A number of studies have shown that water-soluble organic compounds constitute a significant fraction of carbon mass. Previous studies encompassing both urban and rural locations have reported that water-soluble organic compounds accounts for approximately 20% to 67% of the total particulate carbon in the atmosphere (Decesari *et al.*, 2000; Sempere and Kawamura, 1994; Muller *et al.*, 1982, Cadle and Groblicki, 1982). Recent studies in Hong Kong 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).

The WSOC composition remains poorly characterized. Observations regarding the molecular composition of the water-soluble organic compounds 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 (C₂-C₉), ω -oxo-carboxylic acids (C₂-C₉), pyruvic acid, and α -dicarbonyls (C₂-C₃) 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 compounds 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 (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).

1.6 Study Design

1.6.1 The 12-month PM Study

While a preliminary picture of the fine particle situation in Hong Kong is emerging, based on the 6-month study conducted by EPD and other researchers in Hong Kong, the speciation information of organic carbon remains unclear. A more comprehensive study on PM_{2.5} with the emphasis on organic compounds characterization is needed. To this end, an ad hoc twelve-month study entitled "12-month PM_{2.5} Study in Hong Kong" is conducted to ascertain and characterize the organic species in PM_{2.5} in Hong Kong. Organic species types to be investigated are VOCs, PAHs including M-quarterphenyl, n-alkanes, fatty acids, and alkanols in order to have a better understanding of the sources of these organic compounds.

The sampling locations for the 12-month PM chemical speciation project are Tsuen Wan, Mong Kok, and Hok Tsui selected to represent urban, roadside, and rural environment in Hong Kong, respectively. Details about characteristics of sampling locations, traffic volume, and description of type of cooking or sources near the sites are provided in Table 2. Essentially, intensive sampling was carried out on a six-day cycle from November 2000 to October 2001 at the three locations. The sampling frequency and analytical approaches are detailed in a summary Table 3. In order to collect sufficient filters for subsequent chemical analysis, two samplers were installed in each sampling location. 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. Teflon filter samples collected on day 2 were analyzed for mass, elemental composition, and quartz filters collected on the same day was examined for major soluble ionic species, such as soluble potassium, soluble sodium, nitrate, sulphate, and elemental and organic carbon concentrations. Filter samples (all quartz) 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. Vapor-phase monitoring of VOCs, PAHs, dioxins, and PCBs was performed using SUMMA canister and PUF sampling techniques.

1.6.2 Organics Speciation

Fine particles (PM_{2.5}) smaller than 2.5 μm in diameter may cause adverse health effects and is a major culprit for visibility degradation. Origins of the fine particulates must be identified in order to formulate effective control strategies. Characterization of organic species in fine particulates provides hints on the origins of the fine aerosols.

The main objectives of the SEOC, WSOC, and organic tracer markers investigations included in the present project is to produce a chemical profile for the organic species in Hong Kong's fine particulates and its seasonal variation at the three representative sites. Comparison of data derived from the 12-month particulate matter speciation study shall be made as appropriate. The ultimate goal for the 12-month fine particulates sampling programme is to characterize contribution to fine particulates loading from various sources and subsequently to help formulate effective control strategies. Characterization of climatic conditions to aid the understanding of the fine particulate make-ups and their potential sources is also included.

1.6.3 Solvent Extractable Organic Carbon (SEOC) Study

The Government Laboratory of Hong Kong Special Administrative Region Government was tasked with the job to perform solvent extractable organic carbon analysis for the 12-month PM study. Essential classes of solvent extractable organics such as alkanes, fatty acids, alkanols, and polynuclear aromatic hydrocarbons (PAHs) including M-quaterphenyl was separated, identified, and quantified. Speciation and quantitation of over 100 SEOC were performed using GC/MS technique.

1.6.4 Water Soluble Organic Compounds (WSOC) Study

A research team from the Hong Kong University of Science & Technology is commissioned by HKEPD for the WSOC study and this study augments well with the SEOC study. Water-soluble organic compounds constitute a significant fraction of carbon mass in fine particulates. Recent study has revealed that the water soluble organic compounds (WSOC) accounts for on average 28% of the carbon mass in fine particles at a coastal site in Hong Kong during summer time. While numerous studies have been reported on the characterization of the organic solvent extractable aerosol materials at the molecular level, little has been done to ascertain the chemical nature of the WSOCs.

The primary results from this part of the study will be used for the preparation of chemical profiles of the water-soluble organic compounds and their temporal variation in the fine particulates at three locations in Hong Kong. The findings will lead to a better understanding of the sources and chemical natures of the fine particulates in Hong Kong. The WSOC should complement the SEOC study and facilitate a better understanding of organic speciation of fine particulate in Hong Kong. Specific tasks involved and methodologies employed in the WSOC study included organic anions: ion chromatography; carbohydrates: conversion to formaldehyde followed by HPLC/UV photodiode array detection; amino acids: derivatization followed by HPLC/fluorescence detection; aliphatic amines: derivatization followed by HPLC/fluorescence detection; urea: derivatization followed by colorimetry; oxo-acids: derivatization followed by GC/MS analysis.

1.6.5 Organic Markers Study

In parallel to the 12-month project on chemical speciation for PM, a joint project between EPD and Georgia Institute of Technology is established to facilitate a better understanding of the sources and nature of the organic compounds in particulate matters found in Hong Kong.

Specific tasks entailed in the organic markers speciation study are as follows:

A review of using organic compounds as tracers for source contribution in particulate matters; introduction to the determination of organic compounds in particulate matters: extraction and analytical schemes; organic compounds included in the extraction and analytical schemes are n-alkanes, branched alkanes, cycloalkanes, n-alkanoic acids, n-alkenoic acids, PAH, oxy-PAH, hopanes, steranes, alkanedioic acids, resin acids, aromatic acids as well as key tracer compounds such as levoglucosan; data interpretation and application of organic marker compounds data with OC/EC information for the representation of major sources of carbonaceous aerosol (CMB 7 model) and the understanding of visibility issues.

At the time of preparing this final report, information about the organic marker compounds study is not yet available for inclusion in this report.

1.6.6 Site Locations

While a map depicting the locations of HKEPD ambient air quality monitoring network is given in Figure 1a, a map showing the three sampling sites for the 12-month PM chemical speciation project is given in Figure 1b. Three sampling sites, including five supplemental TEOM sites, were selected to provide a good representation of PM_{2.5} situation in urban, roadside, and rural environments in Hong Kong and to augment the existing ambient air quality monitoring network operated by Hong Kong Environmental Protection Department (HKEPD). The locations of the seven sites (TW sampling site and TW TEOM site occupy essentially the same location) are depicted in Figures 1c to 1i. The sampling schedule and parameters investigated were intended to augment with data obtained in EPD ambient air quality monitoring network and toxic air pollutants monitoring stations.

1.6.7 Summary of Filter Sampling Protocol During 12-month Study in Hong Kong

1. Sampling Sites: Tsuen Wan (TW) represents an urban site, Mong Kok (MK) represents a roadside site, Hok Tsui (HT) represents a background site
2. Filter Sampling Strategy: 2 sets of filters are collected in parallel at each of the locations for these 24-hr durations every six days sampling cycle. Each sampling cycle consists of day-1 (2 quartz filters), day-2 (1 quartz and 1 Teflon filter), and day-3 (2 quartz filters) sampling arrangement as given in Table 3. Therefore, there are 5 sampling cycles (with 15 filter sets) for each month. The sampling flowrate is 16.7 l min^{-1} with an inlet that removes particles greater than $2.5 \mu\text{m}$. Schedules for $\text{PM}_{2.5}$ and TAP sampling are given in Appendix 2.

1.6.8 Definition of seasons in Southern China and Determination of the four Seasons for the Study-period

In meteorology, it is traditional to classify the four seasons spring, summer, fall and winter as the four three-month periods starting from March 1st each year. Nevertheless, many researchers had pointed out that this crude classification should only be used in a very loose sense, and one must take into account the local variability for different places and years. In particular, the World Meteorological Organization (WMO) recommends the use of 30-year averages to define climate. The strong interannual variability of each year's weather is the main reason for requiring such a long period of time in the definition of climate.

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. Because of the intense heating effect of the Tibetan Plateau, the Asian monsoon system is the strongest and one of the most important components in the global circulation. Under the influence of the Asian monsoon, we typically have longer summers and winters and relatively shorter springs and falls in Hong Kong.

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 flow 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.

The seasonal march of the Asian monsoon system is being affected by many different phenomena that have substantial interannual variabilities. These include phenomena like snow-cover over the continent, soil moisture and surface types, sea-surface-temperature in the Indian and Pacific oceans (El Nino), the upper stratospheric quasi-biennial oscillation (QBO), and solar-activity. Interactions between these phenomena can substantially modify the phase of the Asian Monsoon circulation, and in turn can shift, lengthen or shorten the various seasons in any individual year. As a result, it is difficult to just use past records to define the starting or ending time of the seasons in any particular year. Instead, to ensure proper delineation of the seasons for the chemical analysis, this should be done afterwards using the actual meteorological observations.

In this project, the seasonal change patterns of sea-level pressure and upper level wind direction are used to give a rough seasonal division for the study period. The exact division dates are determined by looking for the arrival date of the first *synoptic event* that is typical in the respective seasons.

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 2a, which shows the SLP variations at a weather station in Shenzhen (WMO station number 59493) between 1 May, 1997 and 31 October, 2001.

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. Unlike surface 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 2b, 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 2c). 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 2d shows the time variation of SLP from 1 April 2000 to 23 October 2001. Four periods are selected for 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 2e.

Fig. 2d shows a gradual rising trend of SLP from mid-October to mid-November, and then the SLP remained high for a few month. A more detailed plot in Figure 2e(i) 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 2e(ii)). 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 2e(iii) and Figure 2e(iv)). The division dates were accordingly identified.

In summary, the division dates for the four seasons are as follows:

Winter: 2000/11/5 - 2001/3/13 Spring: 2001/3/17 - 2001/5/16
Summer: 2001/5/19 - 2001/9/20 Fall: 2001/9/21 - 2001/10/31

In addition to using meteorological data to define operational seasons for the study period, wind roses from several wind stations are plotted in Figure 3a to provide an overview of prevailing winds over Hong Kong (HK). These includes wind observations from EPD air quality monitoring stations (AQMS) at Yuen Long (YL), Shatin (ST), Tai Po (TP), Tsuen Wan (TW), Kwai Chung (KT), Central Western (CW), Shum Shui Po (SP), Kwun Tong (KT), Mong Kok (MK), Eastern (EN) and Tung Chung (TC), HK Observatory (HKO) wind stations at Waglan Island (WL), Kings Park (KP), Tap Mun (TM), and HK University of Science and Technology (HKUST) wind station at Tap Shek Kok (TSK). The locations of these stations are shown in Figure 3b. Figure 3a shows that typically winds at the HKO and HKUST sites (WL, KP, TM and TK) are stronger than those at the EPD sites. This is because the EPD AQMS are located in or near build-up areas, while the HKO and HKUST wind stations are located in more opened areas.

More detailed wind roses for WL and TK are shown in Figure 3c. The wind is strongest at WL, which is a remote outlying island at the southeast corner of HK. As the background wind affecting HK is mostly easterly, WL lies in an upstream area of these background winds and outside the wind envelope associated with HK's topography. The wind rose at WL shows that HK is affected most often by background easterlies, and secondly by northeasterlies. There are also times when HK is under influence of background southwesterlies; this usually occurs during the summertime southwesterly phase of the East Asian monsoon (not shown). In contrast, the TK station is located on the western side of HK near the mouth of Pearl River Estuary. The winds at TK are weaker than in WL because they are under stronger influence from local urban, topographic and land-sea breeze effects. In addition, clear diurnal signals can be seen in wind time-series for TK (Figure 3d). Hence, the winds at TK will also be used here to help depict pollutant transports due to local and land-sea breeze effects over the western side of HK.

Pollution roses derived from hourly measurements of NO, NO_x, NO₂, SO₂, O₃, PM₁₀ or Respirable Suspended Particulates (RSP), and PM_{2.5} TEOM (FSP) from the YL, TW, MK and CW stations are used to show transport characteristics of the pollutants over HK. In particular, pollution roses with respect to their local wind, wind at TSK, and wind at WL are plotted in Figs. 3e-3h, 3i-3o, and 3p-3v, respectively. As discussed earlier, while the wind at TK can be used to help depict the local and diurnal wind effects in the western part of HK, the wind at WL is used here to represent the large-scale background

wind. Wind data is not available for Hok Tsui during the study period; wind data from WL can be used as a reference.

Preliminary observations of the pollution roses are summarized as follows:

- Figure 3e. MK is a roadside AQMS, and hence the winds are weak (mostly less than 2 m/s); this suggests that the site is under stronger street canyon and/or urban envelope effects, and the wind direction measured at MK are not representative of the direction of the background or regional winds. W and NW winds at MK are associated higher levels of SO₂, NO, NO_x and PM₁₀. The strongest directional dependence is found in the SO₂ pollution rose, and the least dependence observed in CO. These results suggest that the SO₂ at MK is transported in mostly by local westerly, while the CO is generated mainly locally around the station.
- Figure 3f. TW is a general AQMS and the winds are a little stronger than at MK (but still much weaker than at the HKO stations). Higher levels of PM₁₀, PM_{2.5}, NO, NO₂, NO_x and SO₂ are associated with SW wind at TW. In addition, higher levels of PM₁₀, PM_{2.5} and SO₂ are also associated with W and NW winds, particularly when the winds are stronger (> 4 m/s). Similar to MK, least directional dependence is observed in CO, suggesting again that CO at TW is also likely to be locally generated. Also interesting is that O₃ levels are higher when the wind is stronger, particularly when the wind is N or NW, suggesting that O₃ are mostly transported remotely to the TW site.
- Figure 3g. CW is a general AQMS in the HK island with strong street canyon character; over 50% of the wind being easterly and the second mode is westerly. Higher levels of PM₁₀ and SO₂ are identified with WNW wind, while higher levels of NO, NO₂ and NO_x are found with N wind. For O₃, higher levels are associated with E and W winds along the local topography; the concentration level also increases with stronger wind, suggesting again that O₃ at CW is related to remote transport.
- Figure 3h. YL is a general AQMS in northwestern HK; the winds at YL are slightly stronger than that of TW (less blocking) and there are still clear local canyon effects with the predominant winds being E/NE and S. Higher levels of SO₂, PM₁₀, O₃ and NO₂ are all associated with local WNW winds. In addition, the pollution roses also show that mean concentrations for SO₂, PM₁₀ and O₃ increase with increasing wind speed, suggesting that remote transport is important for controlling the concentration of all these pollutants at YL.

- Figure 3i. Pollution rose for $PM_{2.5}$ at TW with reference to winds at TK show that highest $PM_{2.5}$ concentration is associated with NW and N winds, and lowest $PM_{2.5}$ concentration is associated with S wind. In addition, when the wind is southerly, the $PM_{2.5}$ concentration decreases with speed, but when the wind is northwesterly, the $PM_{2.5}$ concentration increases with speed with maximum concentration when the wind TK is between 4-6 m/s. This suggests that the $PM_{2.5}$ levels at TW are mainly controlled by nearby local emissions when the wind is southerly, and that the $PM_{2.5}$ levels are partly controlled by remote sources when the wind is northwesterly.
- Figure 3j. Pollution roses for PM_{10} at YL, TW, MK and CW with reference to winds at TK show characteristics very similar the one discussed above (for $PM_{2.5}$ at TW). These results show also that factors affecting PM_{10} levels are similar for all four sites (i.e., no indication of very nearby local sources), and that the higher PM_{10} levels at TW are related to remote transport of pollutant from the NW and N directions.
- Figures 3k-n. Pollution roses for SO_2 , NO_x , NO_2 and O_3 at YL, TW, MK and CW with respect to winds at TK also showed that highest mean concentration for these pollutants occur when (1) the winds at TK is NW, and (2) the wind speed is between 4-6 m/s. These suggest that, similar to PM_{10} , remote transport is an important factor contributing to the level of these pollutants at *all these different sites* when the wind at TK is NW.
- Figure 3o. The O_3 levels at the YL and TW increase with wind speed for all wind directions and particularly when the wind is NW, suggesting that O_3 is mostly related to remote transport at these sites. In contrast, the O_3 concentrations at CW are highest when the wind at TK is weakly easterly, suggesting that local effects are significant for the O_3 levels at CW; since CW is located downwind of the main urban centers (i.e., Central, Wan Chai and Causeway Bay) when the wind is easterly, the higher O_3 in this situation is related likely to local photochemical production of O_3 from NO_x produced over in the urban centers.

Figures 3p-v. As explained earlier, winds at WL are much stronger than winds at other stations. The pollution roses with respect to winds at WG are used show the difference in pollution levels with respect to strong or weak background winds from different directions. We found that, stronger winds at WL with southerly components are associated with lower pollutant concentrations (except for O₃), suggesting that local sources are more important when our background winds are southerly. In contrast, when the winds at WG has significant northerly or westerly components, pollutants levels are higher when the wind speed at WG is moderate, which are signatures of more remote sources to the north and west of HK. In the case of O₃, highest pollutant concentrations are associated with the strongest wind, particularly in the east and northeasterly directions. This suggests that, compared with pollutants like SO₂ and PM₁₀, high O₃ concentrations are related spatially to a much larger scale problem, and that the location with the highest O₃ concentrations in a regional perspective is likely to the east or northeast of HK.

EXPERIMENTAL

2.1 Filter-based FRM Sample

In order to provide a consistent set of fine particulate filters for gravimetric and chemical speciation analysis, R&P Partisol Plus Model 2025 – one of the USEPA designated FRM samplers were operated simultaneously at each site. The Partisol samplers were equipped with an Andersen SA-246 size-selective inlet/WINS impactor to sample PM_{2.5} at a flow-rate of 16.7 L/min. At this flow-rate, a nominal volume of 24.1 m³ of ambient air would be sampled over a 24-hour period. A vacuum pump drew ambient air through the inlet and down through the filter. The flow-rate was controlled by a mass flow controller, downstream of the sample filter, and thus not affected by filter loading. For day-2 of the 6-day sampling cycle, one Partisol sampler collects aerosol samples on Teflon filters for determination of mass and trace elements (Na - U), while the other Partisol used quartz-fiber filters for subsequent determination of ions (K⁺, Na⁺, Cl⁻, SO₄⁻, NO₃⁻, and NH₄⁺), OC, and EC. For day-1 and day-3 of the 6-day sampling cycle, additional 47-mm quartz-filters were collected using the two samplers for solvent extractable organic compounds (SEOC), water soluble organic compounds (WSOC) and organic tracer marker compounds studies (see also Table 3 for further details).

A schematic diagram for the R&P Partisol Plus Model 2025 is depicted in Appendix 3. The R&P Partisol Plus Model 2025 is designed to meet the regulatory monitoring requirements for PM-2.5 sampling in the U.S. One Partisol sampler uses a Teflon filter to obtain PM_{2.5} mass and trace elements (Na - U). The second Partisol sampler uses a pre-baked quartz filter that is split in half after sampling with one half being

analyzed for OC, EC and ionic species at Desert Research Institute for water-soluble chloride, nitrate, and sulfate by ion chromatography (IC), ammonium by automated colorimetry (AC), and sodium and potassium by atomic absorption spectrophotometry (AAS) and the other half by Government Laboratory for the same parameters for inter-lab comparison purposes.

Potential sampling artifacts associated with the collected sample may be resulted from filter-based samplers and filter media are well documented (Solomon et al., 1988, Hering et al., 1988; Hering and Cass, 1999; Eatough et al. 1989, Koutrakis, P, 1998, USEPA, 2000, Chow,1995, Chow et al, 1996, Lee and Ramamurthi, 1993, Lippmann, 1989, Pang et al, 2002, Turpin et al, 1994, Watson and Chow, 19933). Several recent publications have examined various properties of the PM_{2.5} FRM (Chow et al., 2002, Chung et al., 2002, Eisner and Wiener, 2002, Kenny et al., 2000, Musick, 1999, Noble at al., 2001, Pang et al., 2002, Peters et al., 2001, Pitchford et al., 1997, Poor et al., 2002, Skinner, 1990, Tanner and Parkhurst, 2000, Tropp et al., 1998, U.S.EPA, 1997, U.S.EPA, 1998a, U.S.EPA, 1998b, Vanderpool et al., 2001, Watson and Chow, 2002a, Watson et al, 1998, Peters et al 2001, a, b, c, d). Nevertheless, the FRM/TEOM comparisons show that the Hong Kong PM_{2.5} is relatively stable and that the FRM samples reasonably represent what is in the atmosphere.

2.2 Real-time PM sampler

In order to supplement PM_{2.5} concentration information in Hong Kong during the study period, data from the TEOM Series 1400a Monitor fitted with a PM_{2.5} inlet as a real-time device for measuring the concentration of particulate smaller than 2.5 µm diameter in ambient air is included in this report. TEOM PM_{2.5} monitors are installed at 5 locations in Hong Kong and these sites are Tsuen Wan (TW) [represents urban/commercial/residential surroundings], Tap Mun (TM) [represents background surroundings], Tung Chung (TC) [represents new town surroundings], Causeway Bay (CB) and Central (CL)[represents roadside and commercial surroundings]. Real-time PM_{2.5} concentrations monitored by the TEOM monitors at these 5 locations are used to augment the data set obtained in the 12-month PM speciation study. Typical sampling configuration for the TEOM monitor is given below:

Flow Rate Through Sample Inlet	16.7 L/min (1 m ³ /hr)
Main Flow Rate	3 L/min
Temperature of Sample Stream	50° C
Particulate Concentration	less than 5 µg/m ³ to several g/m ³

2.3 TAP Sampling Methods Applied in this Study

The following TAP sampling and analytical methods are applied in the present study:

- Volatile Organic Compounds (VOCs) with the Xontec Model 910A canister

sampler followed by GC analysis according to U.S. EPA Method TO-14A.

- Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) with an Andersen GPS1X PUF sampler fitted with an 8"x10" particulate filter followed by solvent extraction and HRGC/HRMS analysis using isotope dilution techniques as described in USEPA method TO-9A.
- Polycyclic aromatic hydrocarbons (PAHs) sampled with an Andersen GPS1X PUF sampler followed by solvent extraction and GC/MS analysis according to USEPA method TO-13.
- Polychlorinated biphenyls (PCBs) with a GPS1X PUF sampler followed by solvent extraction and GC/ECD analysis according to the USEPA TO-4 method.
- Carbonyls with a Xontec 925 sampler on silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) (Arnts and Tejada (1989)) followed by extraction and HPLC analysis according to USEPA TO-11A method.
- Hexavalent chromium with a Xontec 920 filter sampler on bicarbonate impregnated filters followed by extraction and ion chromatographic analysis by California Air Resources Board's 039 method.

2.4 Chemical Speciation and Chemical Analysis

Where applicable, the methodologies employed for the determination of major ions and elements of PM_{2.5} are similar to those specified for the National PM_{2.5} Chemical Speciation Network (EPA, 1998) and Chemical Speciation Guidance Document (Chow and Watson, 1998, Chow et al 1993a, Pace, 1998). The basic set of parameters used for the chemical characterization of PM_{2.5} particulate include mass, sulfate, nitrate, and ammonium ions, elements (Na through U), organic carbon (OC) and elemental carbon (EC) (Chow, 1995, Chow et al 1993b, Chow et al 1994, Chow et al 1996). Filter media, Teflon (47-mm Teflon Membrane Filter [PTFE] with a polymethylpentane support ring, Model No. R2PJ047, Pall Gelman) and quartz (47 mm Quartz [QMA] Filter, Model No. 1851047, Whatman) filters used in this study were designed for chemical analysis by routine methods as described in the Guideline on Speciated Particulate Monitoring (Chow and Watson, 1998), Koutrakis (1998), Chow and Egami, 1997, Chow et al, 1996). Chemical analysis of aerosol on the collected filters is performed by routine methods as described in USEPA (1998) and Chow (1996, 1997, 1998). A summary of parameters determined is given in Table 3. Appendices 3 & 4 summarize all the standard operating procedures (SOP) employed by Hong Kong Environmental Protection Department (HKEPD) and Government Laboratory (GL). Essentially, PM_{2.5} mass is determined gravimetrically on Teflon filters. Elements (Na – U) are determined on the same filter as PM_{2.5} mass by energy dispersive X-ray fluorescence (XRF). Anions (sulfate and nitrate) and ammonium ion are determined from aerosol collected on

quartz-fiber filter media. Organic and elemental carbon (OC/EC) are determined on the quartz-fiber filters using thermal-optical reflectance (TOR) and thermal-optical transmittance (TOT) methods by DRI and GL respectively.

The following sections provide a brief description of the sample collection and chemical analysis methods used in this study by species.

2.4.1 PM_{2.5} Mass Measurement

PM_{2.5} mass is determined gravimetrically on Teflon filters using a Mettler Toledo MT-5 microbalance following procedures outlined in the HKEPD's SOPs in Appendices 3 & 4. Prior to sampling, filters are equilibrated for at least 24-hr at 20-23°C and relative humidity (RH) between 30% and 40% and then weighed, sealed in Petri dishes, labelled, and sealed in anti-static Ziplock bags. Sampled filters are equilibrated for at least 24-hr at 20-23 °C and relative humidity between 30% and 40% before weighing. PM_{2.5} mass is determined by the difference between weight of the post- and pre-sampling filters. Ambient PM_{2.5} concentrations are determined by dividing the mass per filter by the actual volume of air sampled. A summary of filter weighing QA/QC results is given in Table 4a. Basically, the filter weighing procedures adopted in the present project are developed in accordance with USEPA filter weighing guidelines for PM_{2.5}.

2.4.2 Trace Elements (Na-U)

Teflon filters analyzed for gravimetric mass are also analyzed for trace elements from Na to U using X-ray fluorescence (EDXRF) method (Chow, 1995, Chow 1998, Watson et al, 1999). In this method, the filter is surrounded by an atmosphere of helium gas. Secondary x-rays are used primarily as the excitation source resulting in virtually no heating of the filter or collected sample. Quantification of EDXRF spectra are obtained by comparing to standards of known concentration as described in the SOP issued by DRI (Chow, 1995, DRI SOP 1994b). Atmospheric concentrations are obtained by dividing the loadings per filter, usually in nanograms (ng) by the actual volume of air sampled.

2.4.3 Sulfate, Nitrate, and Ammonium Ions

Sulfate, nitrate, and ammonium ions are determined in filter extracts from quartz-fiber filters by ion chromatography (IC). Quartz filters (Whatman) pre-baked at 900°C were used for sampling and ion analysis. Anions (i.e. sulfate and nitrate), ammonium ion, and cations (e.g. potassium and sodium), and ammonium ions are determined from the quartz filters. Both DRI and GL conducted analyses for these water soluble ions for interlaboratory comparison purposes.

2.4.4 Organic and Elemental Carbon

The methods currently being applied for the determination of organic and elemental carbon in particulate filters are operationally defined and it is currently a popular subject of investigation owing to the important roles carbon play in atmospheric

chemistry and policy formulation.

A major uncertainty in determining total carbon (TC) using thermal evolution methods results from differences in volatilization of certain organic compounds during sampling and storage (Fitz, 1990; Chow et al., 1996, Watson et al 2001, Watson et al 1994, Watson and Chow, 1994, Watson and Chow, 2002a, Watson and Chow, 2002b). The split of organic and elemental carbon in thermal analysis is even more ambiguous because it depends on temperature setpoints and a number of operating parameters, and these parameters are only empirically defined. To overcome this problem, a laser is used to monitor changes in filter darkness during the thermal evolution process by detecting either filter reflectance (thermal/optical reflectance [TOR] or transmittance (thermal/optical transmittance [TOT]) method.

While the National Institute of Occupational Safety and Health (NIOSH) 5040 method (NIOSH, 1996, 1998, 1999) employs TOT for OC/EC determinations, two analytical protocols, IMPROVE and STN, are used in thermal evolution analysis of TC, OC, and EC in the US National Park Service's IMPROVE network and in USEPA's Speciation Trends Network (STN), respectively. The STN protocol is similar to the NIOSH protocol (NIOSH, 1996, 1998, 1999) except that temperature and combustion time are different for high-temperature carbon, whereby the temperature is reduced to ~600 °C before a He/O₂ atmosphere is introduced. Besides the temperature protocol, another major difference between IMPROVE and STN is the residence time at each temperature setpoint. The IMPROVE protocol requires the FID signal to return to baseline before advancing to the next setpoint, but the combustion duration at each setpoint is fixed in the STN protocol. In the present study, both TOR and TOT methods were employed for the analysis of organic carbon and elemental carbon in the PM_{2.5} particulate. OC and EC collected on pre-baked quartz-fiber filters were determined by DRI and Government Laboratory using the TOR and TOT methods respectively (see also Appendices 6). In the TOR method, a portion of the quartz-fiber filter sampled by a precision cutter is heated first in a stream of helium (He) as carrier gas in a pre-determined temperature programme to extract organic material from particulate matter. This is followed by the addition of a stream of 2% oxygen in He for the oxidation of elemental carbon. The volatilized carbonaceous material is first converted to CO and then to methane, which is detected by a flame ionization detection method for carbon quantitation. In the TOT method, organic carbon compounds collected on quartz filters are vapourised under a stream of He. They are oxidised to carbon dioxide at 870°C using manganese dioxide. The carbon dioxide is reduced to methane for quantitation by flame ionization detector (FID). Residual elemental carbon on the filters is oxidised to carbon dioxide in the presence of oxygen (2%). Carbon dioxide is then reduced to methane for quantitation by FID. Correction for OC/EC analysis for possible charring during the highest temperature step in 100% He are made for both the TOR and TOT methods. Concentrations are determined by comparison to standards of known amounts. Atmospheric concentrations are obtained based on the amount of filter used and the volume of air sampled. Since the carbon fraction (OC, EC, and other sub-fractions defined by temperature set points,

temperature ramping rates, residence time at each set point, combustion atmospheres, and pyrolysis monitoring by reflectance and/or transmittance) measurement protocols make a difference for the samples. In addition to IMPROVE TOR carbon data, this study reported two different versions of STN TOT carbon data: 1) OC/EC split determined when laser transmittance returns to its initial value regardless of when O₂ is added; and 2) OC/EC split determined either when oxygen is introduced or when laser transmittance returns to its initial value. In essence, for DRI OC/EC measurements, five different versions of EC can be defined: 1) IMPROVE reflectance, 2) IMPROVE transmittance, 3) NIOSH reflectance returning to initial regardless of when O₂ is added; 4) NIOSH transmittance returning to initial regardless of when O₂ is added, and 5) NIOSH after O₂ is added. The nine fractions normally reported by the IMPROVE analysis (OC1, OC2, OC3, OC4, EC1, EC2, EC3, OPR, and OPT) are also worthy of future in-depth examination as their abundances may indicate different source contributions. In particular, the pyrolysis fractions by reflectance (OPR) and transmittance (OPT) may be related to the water soluble carbon contents (Yu et al., 2002).

2.5 Splitting Filters for Multiple Analyses

As described above, some of the filters are used for more than one analysis for various reasons. For example, Teflon filters for elemental analysis were conducted by DRI and GL for comparison purpose (Appendices 6 & 8). Quartz-fiber filters are quartered for different analytical purposes. For further information about arrangement of filters for analysis please refer to Table 3. The SOP for quartz filter cutting can be found in Appendix 9.

2.6 Filter Preparation

While Teflon filters are equilibrated at 20-23°C and RH between 30% to 40% as described in Table 3a., quartz filters used for OC/EC analysis are baked for several hours (Chow, 1995, Chow and Watson, 1998) at 900 °C to lower blank levels to 1 µg C cm⁻² of filter material.

2.7 Sampling Locations and Rationale

Three sampling sites were selected in Hong Kong to augment the existing ambient air quality monitoring network operated by Hong Kong Environmental Protection Department (HKEPD). While a map depicting the locations of HKEPD ambient air quality monitoring network is given in Figure 1a, a map showing the three sampling sites for the 12-month PM speciation project is given in Figure 1b. Table 2 provided details about the sampling sites and five supplemental TEOM sites that are directly relevant for the present study: the site name and address; coordinates; site elevation; elevation of sampling inlets above ground level; a brief description of the surroundings in different direction that includes possible nearby sources; descriptions of type of cooking (e.g. commercial/residential) available air quality measurements; sampling frequencies and durations; and period of record (i.e. when was the site

established). Figures 1c to 1i depicted further information about directional photographs of sites and surroundings, locations of major roadways, a compass marking north for the seven sites already described in Table 2 and section 2.2.

The Tsuen Wan (TW) and Central/Western (CW) sites, (toxic air pollutants [TAP] only), established in July 1997, represent urban/commercial/residential surroundings. Metal degreasing, dry cleaning, and building material manufacturing are among the light industrial activities within 0.5 to 1 km NW and SE of the TW site. A hospital with large heating units and a medical incinerator is 0.1 to 0.2 km N and NNW of the CW site. Monitors at these sites have adequate exposure, with monitoring probes at 17 to 18 m above ground level, on the rooftop of five to six story buildings. Road dust from nearby streets will not make appreciable contributions at this elevation.

The Mong Kok roadside site was established in November 2000 at the junction of the heavily travelled Lai Chi Kok and Nathan Roads. This station intends to represent street-level exposure to pollutants, especially those from nearby vehicle exhaust and road dust. Vehicle types passing this site include commercial buses, vans, taxi, light-duty trucks and passenger cars; both diesel and spark-ignition engines are used in these vehicles. Cooking emissions from numerous restaurants and street-vendors nearby may also affect gas and particle measurements, especially for organic compounds typical of these emissions. Sampling probes are located ~2 m above ground, about the same level at which pedestrians would be exposed to pollutants.

The Hok Tsui (HT) ad hoc sampling site was also established in November 2000 to represent regional concentrations at Hong Kong's southwest boundary facing the South China Sea. Marine aerosol and cargo ship emissions from the South China Sea are the predominant local sources. Transport is typically from the continent during winter and from the ocean during summer, and there are probably diurnal variations in flows associated with land/sea breezes. Sampling probes are on a concrete platform located on a hillside ~60m above mean sea level.

2.8 Program, Sampling, and Analysis Schedules

The overall programme and sampling schedule of the present study is presented in Table 2 & Appendix 2 which are designed to cover a 6-day sampling cycle for a period of 12-month. The sampling work for the project commenced from November 2000 to October 2001. The sampling work of the present project commenced from November 2000 after taking into consideration that high particulate levels are typically found in winter months in Hong Kong.

2.9 Preliminary Evaluation and Training

Upon appointment of contractor (ENSR Environmental International Ltd.) responsible for the PM_{2.5} particulate sampling and TAPs sampling work for the present project, training programme was provided to field personnel for PM_{2.5}

sampling procedures familiarization. The operation of PM_{2.5} samplers were in accordance with SOPs developed by HKEPD based on guidelines issued by the USEPA (USEPA 1997, USEPA 1998). Only those personnel who have passed the examination held by HKEPD will be allowed to carry out the PM_{2.5} sampling work. A list of SOPs used in the present project is given in Appendices 3 & 4.

2.10 Site Installation and Decommissioning

ENSR Environmental International Ltd was commissioned by EPD to perform the sampler commissioning work for both the PM_{2.5} and toxic air pollutants monitoring work under the 12-month PM_{2.5} speciation project. A summary of SOPs pertaining to the sampling, samplers installation and decommissioning work is given in Appendix 3.

2.11 Sampler Operation and Filter Shipping and Storage

The operation of samplers is documented in the SOP developed by HKEPD based on guidelines issued by USEPA (USEPA 1998) and this SOP is given in Appendix 2. Typically, after the filters are weighed by HKEPD's staff in accordance with filter weighing procedures (Appendix 4), sampled filters are stored in refrigerator under 4°C in HKEPD's laboratory prior to shipping the filters to analytical laboratories for chemical analysis. Filter shipping procedures are developed based on DRI's guidelines and SOPs (DRI SOP1994a, DRI SOP1994b).

2.12 System Audit Performed by Prof Judith Chow

A thorough system audit was performed by Prof Judith Chow at the start of the present project, all recommendations are either ratified or to be followed up in future studies. Key recommendation and suggested follow-up items are presented in a system audit report prepared by Professors Judith Chow and John Watson as given in Appendix 5.

2.13 Quality Assurance/Quality Control (QA/QC)

QA and QC establish the precision, accuracy, and validity of measured values. The overall QA/QC programme integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of QA/QC programme are data values with specified precisions, accuracies, and validities. QC is intended to prevent, identify, correct, and or validity of the measurements. Quality auditing consisted of systems and performance audits. The system audit includes a review of the operational and QC procedures to assess whether they were adequate to assure valid data that met the specified levels of accuracy and precision (see also section 2.12). Quality auditing also examined all phases of the measurement activity to determine that procedures were followed and

that operators were properly trained. The performance audits challenged the measurement/analysis systems with known transfer standards traceable to primary standards. While quality control and performance audits were performed by HKEPD (Tables 4a to 4f), systems audit was carried out by Professor Judith Chow (section 2.12).

A thorough QA/QC effort was implemented for this study to ensure the quality of the data. The QA/QC procedures implemented in the present project are developed in accordance with guidelines issued by USEPA (USEPA 1998). These efforts included audits of the samplers prior to, during, and after the commencement of field programme. Laboratory quality assurance and control followed already established procedures and included external audits of the samplers by HKEPD as documented in HKEPD's SOPs (Appendices 3 & 4, QA/QC manual for TAP monitoring programme, 2001).

The QA/QC work for the R&P Partisol sequential samplers are implemented according to the R&P Operation Manual and the USEPA's QA Document 2.12 (USEPA 1998). Details about QA/QC activity and frequency for field sampling work are presented in Table 4b.

A summary of QA/QC information pertaining to the sampling and filter weighing aspects of the project is presented in Tables 4a to 4f. Field blanks were acquired and replicate analyses were performed for ~15% of all ambient samples. Results of performance audits of sampler flow-rates are presented in Table 4f.

2.14 Field QA/QC - The Partisol-Plus Model 2025 Sequential air Sampler

Quality assurance consisted of an initial system audit at the beginning and performance audits at the beginning and each quarter. EPD's staff conducted these audit tasks using independent traceable standards for the 12-month project. Initial QA audit of the sampler was performed prior to the collection of first sample if possible, or as soon as possible after the initiation of the programme. Initial system audits checked installation of the samplers, site setting, site operations and operators, and custody management. Performance audits checked flow rates, check for vacuum leaks, and other performance characteristics of the samplers. Results indicate that all audit parameters complied with the USEPA acceptance criteria (USEPA 1998) during the 12-month project and they are given in Table 4b. Tables 4b & 4c summarize the details of quality control activities, traceability of timer, thermometer, barometer, and volumetric flow.

Quality control was carried out by Contractor, consisting of equipment cleaning, performance checks - time, temperature, and pressure, maintaining appropriate operations logs, and other items as specified on the data log sheets. Essentially, bi-annual multi-point calibrations and monthly one-point check for air flow, temperature and pressure are carried out at sites by the Contractor with relevant traceable standards. The 37 mm filter in the WINS Impactor of each sampler is

replaced upon each field visit subsequently followed with internal and external leak checks. The samplers will then collect three 24-hour samples on three consecutive days according to schedules. All working standards shall be traceable to certified primary standards. Information about calibration parameters including flow-rate, time, temperature, and pressure are given in Table 4c.

2.15 Laboratory QA/QC

Laboratory systems and performance audits were conducted for each species according to schedules already in place in the laboratories (Table 4f). Where applicable, all analytical results have passed all necessary laboratory QA/QC requirements prior to data reporting to HKEPD (Appendix 6).

2.16 Uncertainty for Mass Measurement and Analytical Specifications

Every measurement consists of: 1) a value; 2) a precision; 3) an accuracy; and 4) a validity (Hidy, 1985; Watson et al., 1989, 2001). Measurement attributes as reported by Chow et al., (1993a) for the precision, accuracy, and validity were adopted for the present study. Measurement precisions were propagated from precisions of the volumetric measurements, and the field blank variability using the methods of Bevington (1969) and Watson et al. (2001). However, field blank subtraction was not performed, which is consistent with EPD's data processing procedures for particulate mass measurements. For the present study, the field blank values for Teflon filters were found to be within 30 μg . The flow rate uncertainty was estimated by the average percent difference between the initial and final flow rates (0.84%). A more typical flow rate uncertainty is 5%. The two uncertainties were combined as shown below:

$$\sigma_c = \sqrt{\sigma_x^2 + (0.05)^2}$$

Where σ_x = XRF uncertainty,

σ_c = concentration uncertainty.

A more detailed treatment of calculations pertaining to the precision associated with filter-based measurements is presented in Appendix 6.

Dynamic field blanks were periodically placed in each sampling system without air being drawn through them to estimate the magnitude of passive deposition for the period of time which filter packs remained in a sampler (typically 24 hours). No statistically significant inter-site differences in field blank concentrations were found for any species after removal of outliers (i.e., concentration exceeding three times the standard deviations of the field blanks). The average field blank concentrations (with outliers removed) were calculated for each species on each substrate (e.g., Teflon-membrane, quartz-fiber), irrespective of the sites. As given in Appendix 6, the standard deviation of the field blank is more than twice its corresponding root mean square error (RMSE) for soluble sodium (Na^+) and soluble potassium (K^+).

This may be attributed to contamination to some field blanks during the passive deposition period and during sample changing while exposed to ambient conditions. By examining the individual field blank values, it is shown that these values are well within the range of the standard deviation of the average blank concentrations and therefore are assumed valid and representative (Appendix 6).

Concentrations in $\mu\text{g}/\text{m}^3$ for elements, ions, organic carbon and elemental carbon analysed by DRI are given in Appendix 6 and Table 6. The uncertainty associated with each concentration is a one standard deviation error estimate including both analytical uncertainty and sample flow rate measurement uncertainty. The analytical uncertainty is determined from the counting statistics of the analysis, and represents the precision measure one would obtain from repeated analysis of the sample.

DRI's analytical specifications for the 24-hour $\text{PM}_{2.5}$ measurements obtained in the present study are characterized by minimum detection limits (MDL), root mean squared (RMS) precisions, and lower quantifiable limits (LQL). The MDL is defined as the concentration at which the instrument response equals three times the standard deviation of the response to a known concentration of zero. RMS precision is the square root of the averaged squared uncertainties. The LQL is defined as a concentration corresponding to two times the precision of the dynamic field blank.

Information about analytical uncertainty and a list of proficiency test programmes joined by the air chemistry section of Government Laboratory (GL) is given in Appendix 10.

The following equations calculated the precision associated with filter-based measurements:

$$C_i = (M_i - B_i)/V$$

$$V = F \times t$$

$$B_i = \frac{1}{n} \sum_{j=1}^n B_{ij} \quad \text{for } B_i > \sigma_{Bi}$$

$$B_i = 0 \quad \text{for } B_i \leq \sigma_{Bi}$$

$$\sigma_{Bi} = \text{STD}_{Bi} = \left[\frac{1}{n-1} \sum_{j=1}^n (B_{ij} - B_i)^2 \right]^{1/2} \quad \text{for } \text{STD}_{Bi} > \text{SIG}_{Bi}$$

$$\sigma_{Bi} = \text{SIG}_{Bi} = \left[\frac{1}{n} \sum_{j=1}^n (\sigma_{Bij})^2 \right]^{1/2} \quad \text{for } \text{STD}_{Bi} \leq \text{SIG}_{4Bi}$$

$$\sigma_{Ci} = \left[\frac{\sigma_{Mi}^2 + \sigma_{Bi}^2}{V^2} + \frac{\sigma_V^2 (M_i - B_i)^2}{V^4} \right]^{1/2}$$

$$\sigma_{\text{RMS}_i} = \left(\frac{1}{n} \sum_{j=1}^n \sigma_{Ci}^2 \right)^{1/2}$$

$$\sigma_V/V = 0.05$$

Where:

B_i	=	average amount of species i on field blanks
B_{ij}	=	the amount of species i found on field blank j
C_i	=	the ambient concentration of species i
F	=	flow rate throughout sampling period
M_i	=	amount of species i on the substrate
M_{ijf}	=	amount of species i on sample j from original analysis
M_{jrf}	=	amount of species i on sample j from replicate analysis
n	=	total number of sample in the sum
SIG_{Bi}	=	the root mean square error (RMSE), the square root of the averaged sum of the squared of σ_{Bij}
STD_{Bi}	=	standard deviation of the blank
σ_{Bi}	=	blank precision for species i
σ_{Bij}	=	precision of the species i found on field blank j
σ_{Ci}	=	propagated precision for the concentration of species i.
σ_{Mi}	=	precision of amount of species i on the substrate
σ_{RMS_i}	=	root mean square precision for species i
σ_V	=	precision of sample volume
t	=	sample duration
V	=	volume of air sampled

2.17 Sample Labeling and ID System

A sample labeling system is created for identifying the sample's nature consistently and distinguishing a sample from the others. Each sample is allocated a unique Filter Identity (ID) and Sample ID. Labels were applied onto the lid and the flat part of the base of a PetriSlide to identify each filter. Further information about data format, filter ID, and sample ID can be found in SOP as given in Appendices 3 & 4.

2.18 Quality Assurance & Quality Control Results

As given in Table 4a, all QA/QC activities pertaining to sampling and filter weighing complied with HKEPD's SOPs requirements and well within the USEPA acceptance criteria (USEPA 1998). These QA/QC requirements included environmental conditioning of balance laboratory, accuracy of balance, stability test for lot blank filters, laboratory blank (Teflon) and field blank. Field blanks were acquired and

replicate analyses were performed for ~15% of all ambient samples. A summary of quality control activity and frequency performed for the present study is given in Table 4b. Traceability information relevant for the apparatus used is presented in Table 4c. The acceptance criteria for filter weighing laboratory are presented in Table 4d. The apparatus and materials employed in support of the filter weighing tasks are presented in Table 4e. The environmental conditioning requirements of HKEPD's balance laboratory parameters are mainly dictated by temperature and relative humidity control and they were found to be $21.5\text{ }^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $33.5\% \pm 5\%$. These environmental conditions are well within the USEPA acceptance guidelines: temperature from 20 to 23 $^{\circ}\text{C}$, controlled to $\pm 2^{\circ}\text{C}$; relative humidity from 30 to 40 %, controlled to $\pm 5\%$. Both precision of filter weighing and filter re-weighing are found to be within the $\pm 15\text{ }\mu\text{g}$ acceptance criteria. Precision as determined by collocated sampling with Teflon filters ranged from 0.69 to 4.50 %. These values are substantially lower than the $\pm 10\%$ USEPA acceptance criteria. Although it is not a requirement by USEPA, in the present study, we also determine the gravimetric concentrations for quartz filters: precision as determined by collocated sampling using quartz filters ranged from 0 to 11.7%. The audit results of temperature, pressure, flow-rate, and laboratory comparisons are presented in Table 4f. In general, these results indicated that by ways of audits, performance tests, and laboratory comparisons, the data quality objectives as presented in Table 4a were attained.

2.19 Data Validation

Data validation part of the data processing work can be divided into two parts: Level I and Level II data validation (Chow 1995, Chow 1998, DRI SOP,1994a, Watson et al, 2001, Appendix 6).

2.19.1 Level I data validation

Level I validation entails estimating precisions from replicate and blank analyses, flagging measurements for deviations from procedures (including defining flags that indicate the nature of the difficulty, and identifying and removing invalid values (e.g., when an instrument was not working). Specifically, these steps are: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheet; 3) eliminating values for measurement which are known to be invalid because of instrument malfunctions; 4) replacement of data from a backup data acquisition system in the event of failure of the primary system; and 5) adjustment of measurement values of quantifiable calibration or interference biases.

2.19.2 Level II data validation

Level II data validation takes place after data from field sampling and laboratory analyses have been assembled in a common data set. Level II validation shall examine internal consistency among different data and attempts to resolve discrepancies. It includes comparing a sum of chemical species to mass

concentrations, comparing measurements from different methods (e.g., sulfur from EDXRF with sulfate from IC), comparing collocated measurements, calculating anion/cation balances, examining time series from different sites to identify and investigate outliers, and preparing a data qualification statement. Specifically, these steps include the following:

- 1) The sum of chemical species in a particulate matter sample should be less than or equal to the gravimetric mass of that sample;
- 2) Size segregated particle concentrations should be less than total particle concentrations (i.e. $PM_{2.5} < PM_{10}$);
- 3) The sum of all major species (with oxide forms included) should exceed 75% of the measured mass: and
- 4) Analyses of the same species by different methods should yield compatible results (e.g., sulfur by XRF and sulfate by IC);
- 5) Collocated measurements should yield comparable results:
- 6) the ratio of anion concentrations in $\mu\text{g}/\text{m}^3$ to cation concentrations should be 0.8 to 1.2. Further information about validated chemical speciation data can be found in Table 6; Levels I & II procedures employed by DRI on chemical speciation data are given in Appendix 6.

Level I validation flags and comments are included with each data record in the database as documented in Appendix 6 and Level II validation tests evaluate the chemical data for internal consistency. In the present study, Level II data validations were made for: 1) sum of chemical species versus $PM_{2.5}$ mass, 2) physical consistency, 3) anion and cation balance, and 4) reconstructed versus measured mass. Correlations and regression statistics were computed and scatter plots prepared to examine the data. The overall validation results indicate that the data subjected to both Levels I & II validation procedures are valid for further interpretation.

3 RESULTS

3.1 Chemical Characteristics of $PM_{2.5}$

3.1.1 Chemical Components Reported in the 12-month PM Chemical Speciation Study Database

$PM_{2.5}$ particulate matter was collected on R&P Partisol samplers as discussed in previous sections. Mass, major and trace chemical components, organic speciation determination were performed on filters collected during the 12-month study period from October 2000 to November 2001. Methods employed for the present study are described under Introduction and Experimental sections. As shown in Table 3, characterization of Teflon-membrane filter collected particles for mass analysis by gravimetry and elemental analysis (40 elements including Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pb, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb,

and U) by x-ray fluorescence (Watson et al., 1999). The quartz-fiber filter, also a 47-mm diameter filter, was analyzed for mass by gravimetry, for chloride (Cl⁻), nitrate (NO₃⁻), and sulfate (SO₄⁻) by ion chromatography (Chow and Watson, 1999), for ammonium (NH₄⁺) by automated colorimetry, for water-soluble sodium (Na⁺) and potassium (K⁺) by atomic spectrophotometry, and for carbon by two thermal evolution methods.

Excluding field blanks and laboratory blanks, a total of 1080 filters were sampled for the present project and details of valid and void samples are given as follows:

- (i) For the Tsuen Wan site a total of 360 filters were collected: 353 valid samples (294 QMA, 59 Teflon); 7 void samples (6 QMA samples, 1 Teflon sample);
- (ii) For the Mong Kok site a total of 360 filters were collected: 358 valid samples (298 QMA, 60 Teflon); 2 void samples (2 QMA);
- (iii) For the Hok Tsui site a total of 360 filters were collected: 356 valid samples (297 QMA and 59 Teflon); 4 void samples (3 QMA, 1 Teflon).

Overall, close to 99% of sampled filters are found to be valid for gravimetric and analytical determination.

Mean mass concentrations of PM_{2.5} at Tsuen Wan (TW), Mong Kok (MK), and Hok Tsui (HT) for four seasons in Hong Kong were found to be in the range of 26 - 44, 51 - 69, and 15 - 32 µg/m³. In terms of mass concentration levels and assigning the sites in descending order with site characteristics, it is observed that Mong Kok>Tsuen Wan>Hok Tsui or roadside>urban>rural. Figure 3 and Table 4a depict PM_{2.5} levels using filter based measurement method in Hong Kong at Tsuen Wan, Mong Kok, and Hok Tsui, for the representation of urban, roadside, and rural sites respectively. The annual averages PM_{2.5} concentrations at TW, MK, and HT were found to be 34, 58, and 24 µg/m³ respectively. Figure 4 and Table 6 show similar patterns of PM_{2.5} levels using continuous PM_{2.5} measurement method (TEOM): Causeway Bay and Central representing roadside sites>Tsuen Wan and Tung Chung representing urban and new town sites> Tap Mun representing background sites. There is one caveat about PM_{2.5} data comparison: the roadside site at Mong Kok, Causeway Bay and Central have much higher PM_{2.5} values owing to their proximity to nearby traffic. Therefore, when comparing with any kind of PM_{2.5} ambient air quality standards data from urban, new town, and rural stations including Tsuen Wan, Tung Chung, Hok Tsui, and Tap Mun should be used. Since the present project covers a period of 12 months, annual averages can be derived from both filter base measurements and TEOM PM_{2.5} data for the evaluation of PM_{2.5} levels in Hong Kong. The use of TEOM information to gauge the PM_{2.5} levels in Hong Kong have been established in Tsuen Wan by using both quartz and Teflon filters. As shown in Figure 5, both quartz and Teflon filters yield correlation results with TEOM monitor: R² are 0.97 and 0.96 for correlating TEOM data with values determined by quartz and Teflon filters respectively. Therefore a comparison of PM_{2.5} concentrations between filter base measurement by Partisol sampler and TEOM can be made. Indeed, the good comparison between TEOM and filter samples means that these 24-hour averages can be treated interchangeably. Further comparison of PM_{2.5} trends at urban site (Tsuen Wan), rural sites (Tap Mun and Hok Tsui), and roadside sites

(Causeway Bay, Central, and Mong Kok) are presented in Figures 6a, 6b, and 6c. An overall comparison of urban/new town site (Tsuen Wan, Tung Chung), rural/background (Tap Mun, Hok Tsui), and roadside sites (Causeway Bay, Mong Kok, and Central) by seasons is depicted in Figure 6d. Again a similar pattern of concentration levels is found:roadside>urban/new town>rural/background.

3.1.2 Summary Data

Overall summary Tables 5a to 5b and Tables 6a to 6f list for each site 1) each species measured during the 12-month PM sampling period (this include filter analysis results as well as the TEOM, gas measurements (ozone, oxides of nitrogen, sulphur dioxide, and carbon monoxide), compliance PM; 2) its average concentration (averaging periods that correspond to the composite samples used for organic analysis sample compositing, which is seasonal and annual); maximum concentrations and dates on which they occurred (for 24-hour samples and annual averaging periods), and 3) number of samples in the average. This kind of information should be very useful for guiding the discussion of similarities and different source contributors as a prelude to more quantitative source to be addressed in follow-up data analysis.

3.1.3 Integrated Database

Lioy et al. (1980), Chow and Watson (1989), Watson and Chow (1992), and Chow and Watson (1994) summarize the requirements, limitations, and current availability of ambient and source databases in the United States. As the data obtained in this study are intended for further data analysis and modeling applications (Paatero, 1998, Paatero, 2000, Henry, 2000, Watson et al, 1997, Watson et al, 1998, Watson et al, 2002), therefore documentation with regard to sampling and analysis methods, quality control/quality assurance procedures, accuracy specifications, precision calculations, and data validity is provided in this report. The HKEPD 12 month PM study data set intends to meet these requirements. The data files for the present study have the following attributes:

- They contain the ambient observables needed to assess source/receptor relationships.
- They are available in a well-documented, computerized form accessible by personal computers.
- Measurement methods, locations, and schedules are documented.
- Validation flags are assigned.

An integrated database with documentation and description is prepared for the study. This summary information is presented in Table 7. This integrated database is constructed in Microsoft Access with: 1) a site table that included the coordinates, 2) a variable table that contains the mnemonic, the species measured, and the reporting units, and 3) data table that includes the site code, start and stop times, data value, data precision, validation flag, and validation level. Detailed hourly, 24-hour, and seasonal

averages are presented in separate tables to facilitate comparisons. Different measures of the same variable (e.g., OC and EC) will be assigned different mnemonics and definitions.

Presented in Tables 8a to 8d are descriptions of variables for analytical data, filter weighing, toxic air pollutants, and gaseous air quality pollutants. Other related parameters monitored by HKEPD and species measured by DRI have been introduced before (Tables 5a and b) and the DRI data are presented in Table 9.

Data contained in different database files can be linked by indexing on and relating to common attributes in each file (Tables 8a to d). Sampling site, sampling hour, sampling period, particle size, and sampling substrate IDs are, typically, the common fields among various data files that can be used to relate data in one file to the corresponding data in another file. To assemble the final data files, information was merged from many data files derived from field monitoring and laboratory analyses by relating information on the common fields.

3.1.4 Meteorological Data

To aid further data interpretation, relevant available meteorological data are integrated into the data set. More site specific measurements of wind speed, direction, and temperature would allow TEOM and other hourly measurements to be presented as pollution roses and classified by wind speed. This would provide indication for source directions throughout the day (see also section 1.6.8 for further details).

3.1.5 Chemical Components in PM_{2.5}

Mean concentrations of PM_{2.5} mass and chemical components as measured by the Partisol samplers are given in Table 9. Mass and trace elements were determined from the sample collected on the Teflon filter, while ions and OC/EC, solvent extractable organic compounds, water soluble organic compounds, and organic tracer markers analysis were determined from the sample collected on the quartz filter. Details of the filter sampling cycle and PM speciation arrangement are given in Table 3.

Since the main focus of the present study is on chemical speciation of PM_{2.5} particulate, both samples Teflon and quartz filters were subjected to an extensive array of chemical analysis in support of subsequent data interpretation. A more thorough discussion and interpretation of chemical characteristics of PM_{2.5} mass and composition observed during the present study are given in the reports in Appendices 6, 8 to 10 and papers to be written up for the project.

Depicted in Figures 7 to 8 are Box and Whisker plots of major ions and carbon using annual speciated concentrations. These plots show the average, median, 25%, 75%, 5%, and 95% values observed in the data base. Elevated sulfate and organic carbon concentrations are observed in all three sites. High carbon concentrations found at the Mong Kok roadside site may be attributed to vehicular emission sources. Annual average PM_{2.5} mass, sulfate, ammonium, nitrate, organic carbon, elemental carbon, iron, and calcium concentrations are presented in Figures 10a to 10h as frequency distribution

plots. Of particular interest of these plots is the sulfate ion frequency distribution plot: the sulfate distribution plot shows that while there is a small but distinguishable contribution of sulfur from vehicular emission sources from roadside, the overall sulfate ion concentration in PM_{2.5} is almost independent of locations. This sulfate distribution pattern may be indicative of sulfate as secondary aerosol originated from regional sources.

While analyses of elements using XRF for a more comprehensive set of elements are performed by DRI (Table 9), a selected set of trace species was determined by GL (Appendix 10). In general, the results on elements include Al, Si, K, Ca, Fe, Ni, Cu, Zn, Mn, and Pb from GL compare well with DRI. The reasoning for selecting this set of elements for comparison are: 1) these elements were the most likely to be detected above the limits of detection most of the time. 2) measurements of these elements will be utilized as input parameters for the evaluation of percent contribution of major species to the PM mass. Nevertheless, for overall reporting and trends illustration purposes for the present study, analytical data from DRI will be used. The complete database for elements, ions, OC/EC analyses performed by DRI and GL are presented in Tables 10 to 26 and Appendix 10, respectively. A correlation investigation between analytical database from DRI and GL was made and the correlation coefficients between the two data sets are given in Appendix 10. With the exception of soluble sodium and chloride, good correlation results were found for Al, Si, S, K, Ca, Fe, Ni, Cu, Zn, Mn, Pb, K, TC, ammonium, nitrate, and sulfate. Relatively poor correlation results between DRI and GL for soluble sodium and chloride are attributed to the difference in reporting values close to detection limits.

Chloride and soluble sodium were detected in 64% and 93% of all the samples, respectively. Several transition metals (e.g., Co, Y, Mo, Pd, Ag, Cd, In, Sb, La, Au, Tl, and U) were not detected in most of the samples (less than 15%). This is typical for urban and non-urban sites in most regions. Residual-oil-related species, such as nickel (Ni) and vanadium (V), were detected in 98% and 88% of the samples, respectively. Industrial-source-related toxic species such as mercury (Hg) and cadmium (Cd) were only detected in 2% and 13 % of the samples, respectively. Arsenic (As) and selenium (Se) were found above the method detection limits (MDLs) in 77% of the samples. The maximum arsenic (As) concentration of 0.0496 µg/m³ is a relatively high value, being over 20 times higher than the maximum concentration measured during the 2000-01 Southern Nevada Air Quality Study (SNAQS, Green et al., 2002) in the U.S. Motor-vehicle-related species such as bromine (Br) and lead (Pb) were detected in 100% and 97% of the samples, respectively.

Soluble potassium (K⁺) was acquired by atomic adsorption spectrophotometry (AAS) analysis on quartz-fiber filters, and total potassium (K) was acquired by XRF analysis on Teflon-membrane filters. K⁺ concentrations were found to be low to moderate throughout the study area and the majority (90%) of the total potassium is in its soluble state. The average ratio of K⁺/K was 0.80 ± 0.10. Although vegetative burning is not practiced in Hong Kong, the higher K⁺/K ratios imply that combustion sources similar with vegetative burning or long-range transport of wildfire emissions are prominent in

Hong Kong.

The most abundant species found in PM_{2.5} particulate in Hong Kong were nitrate, sulfate, organic carbon, elemental carbon, and ammonium (Tables 14 to 25). One way to illustrate the overall material balance or chemical composition in the PM_{2.5} particulate is to account for other species including crustal, soluble sodium and potassium, and trace species. And a typical approach to obtain a rough mass balance of the sampled PM_{2.5} particulate is obtained by adjusting OC for missing hydrogen and oxygen atoms to obtain organics (or organic matter) and major elements including Al, Fe, Ca, and Si for missing oxygen atoms. Organic matter is obtained by multiplying a conversion factor of 1.4 to OC account for unmeasured oxygen and hydrogen. Other species including Fe, Ca, and Si are adjusted by multiplying by 1.43 for an estimate of Fe₂O₃, 1.4 for an estimate of CaO, and 2.14 for an estimate of SiO₂, and 1.89 for Al (Solomon et al., 1989, Chow and Egami 1997). While crustal material is estimated the summation of Fe, Ca, Al, and Si oxides, other species are used directly without applying any adjustment factors (Solomon et al. 1989, Chow and Egami, 1997). At all sites, the crustal material was found to represent only a small fraction of the total mass, ranging from only 0.6 to 2.2 µg/m³ or about 3% to 8% of the measured mass. Presented in Figures 11 a to d are bar charts and pie charts representation of material balance calculation for chemical components measured for the PM_{2.5} particulate. These charts show species composition for the four seasons, ammonium sulfate, organics, and elemental carbon are the most abundant species found at all the sites. Water-soluble sulphate (SO₄²⁻) was measured by ion chromatography (IC) analysis on quartz-fiber filters, and total sulphur (S) was measured by x-ray fluorescence (XRF) analysis on Teflon-membrane filters. The ratio of sulphate to total sulphur should equal “3” if all of the sulphur were present as soluble as soluble sulphate. A good correlation ($r > 0.98$) was found among PM_{2.5} sulphur/sulphur measurements with an average ratio of 2.74 ± 0.24 . The overall sulphate and sulphur comparison results in the present study support the contentions that more than 90% of sulphur was present as soluble sulfate in the atmosphere. Using stoichiometric ratios of the different ammonium compounds (i.e., ammonium nitrate, ammonium sulfate, and ammonium bisulfate), ammonium bisulfate may account for less than 12% of the total sulphate. The annual mean concentration of ammonium sulfate, organics, and soot (elemental carbon) in the range of 11.9 to 12.7, 5.9 to 22.2, and 1.7 to 19.3 µg/m³ are measured at Mong Kok, Tsuen Wan, and Hok Tsui. Further information can be found in analytical data tabulated in Table 6.

A summary of mean species concentrations for all sites are given in Tables 26 a to c. While the highest mean species concentration (sum of ammonium sulfate, ammonium nitrate, organics, and elemental carbon) for all sites is found in February 2001 (winter month), the lowest species concentration is found in June 2001 (summer month).

As continuous PM₁₀ TEOM data for the present monitoring period is available at the Tsuen Wan site, the percent ratios of PM_{2.5} over PM₁₀ are determined and they ranged from 66% to 78% for the four seasons.

3.2 Statistical Analysis

3.2.1 Time Series Analysis

Time series plots of all major ions, species, and mass concentration are given in Figures 12 a to j, 13 a to c, and 14 a to j. These species were chosen as they represent the major components of the PM_{2.5} mass. Although considerable variability of concentration levels were found for organic and elemental carbon, soluble chloride, nitrate, soluble potassium, soluble sodium, sulfate, calcium, iron, and silicon exhibited similar trends and concentration levels. Given in Figures 15 a to i are time series plots of elements at each site by month. Presented in Figures 16 to 30 are plots of species concentrations versus stations and seasons. These plots are useful for easy reference and aid episode case analysis and establishing trends for patterns for species distribution. Based on the patterns distribution of these species three main features are observed: PM_{2.5} chemical composition is dominated by ammonium sulfate, organics, elemental carbon, ammonium ion and nitrate; species concentrations at roadside > urban > rural; winter > summer and spring > fall.

3.2.2 Regression Analysis for Carbon

3.2.2.1 TOT versus IMPROVE TOR

While annual mean concentrations for organics at Mong Kok, Tsuen Wan, and Hok Tsui are 22.2, 12.2, and 5.9 µg/m³, annual mean soot concentrations are found to be 19.3, 5.4 and 1.7 µg/m³ respectively during the four seasons covered by the 12-month monitoring period. Regression analysis for OC, EC, and TC are performed and graphical representation of these plots are given in Figures 31 to 34 (see also OC, EC, and TC data tabulated in Tables 10 to 11). Since filter weighing was also performed on quartz filters, gravimetric values derived from quartz filters are available for correlation analysis. In general, with the exception of elemental carbon, reasonable correlation between mass concentration with OC or TC are obtained at the Tsuen Wan and Mong Kok sites. In contrast, reasonable correlations were obtained between mass concentration derived from the Hok Tsui site with OC, EC, and TC. Although a clear explanation of these kinds of correlation patterns is not available, it seems that the correlation relationship is elemental carbon concentration dependent. An additional check with mass concentration correlation using values derived from Teflon revealed the same patterns as quartz filters and these correlation plots are given in Figures 32 a to r. Plots of carbon concentrations as determined by TOR (analysis performed by DRI) and TOT (analysis performed by GL) methods for OC, EC and TC are given in Figures 34 a to i. While reasonable agreement are obtained between TOT and TOR correlations, significant variability is observed for EC correlation. Further information about correlations between TOT and TOR can be found in Tables 10 & 11. The interlaboratory results were found to be in line with previous comparisons between TOT and TOR results. Results on TC agree very well ($R^2 = 0.99$).

3.2.2.2 IMPROVE Protocol versus STN Protocol for Carbon Measurements

TC, OC, and EC determined by IMPROVE TOR and STN TOT methods for samples from each and all sites combined are compared and presented in Appendix 6. Although there are currently two versions of the STN TOT methods (i.e., STN TOT (i) and STN TOT(ii)), STN TOT(i) is the default protocol currently used in the USEPA Speciation Trends Network. In most of the cases, all three methods yield similar TC (<10% difference). At the TW (urban) and HT (rural) sites, IMPROVE TOR generally produced higher EC and lower OC than STN TOT(ii), and this agrees with the findings in Chow et al. (2001). STN TOT(i), which relies on optical correction for OC/EC split, tends to yield results closer to IMPROVE TOR. At the MK (roadside) site, ambient concentrations of EC and OC were much higher which mainly due to emissions from vehicular traffic, results from the IMPROVE and STN protocols are poorly correlated. The STN methods seem to overestimate EC when filters are heavily loaded. Overall, the adoption of different analytical protocols can yield significantly different OC and EC measurements, and this will influence the OC/EC partitioning in carbonaceous material.

3.3 Episodes Case Study

3.3.1 Dust Episodes

Yu (Appendix 9) revealed that the two dust episodes occurred in Hong Kong might be of particular interest for PM study. While the first dust episode event occurred from 8 to 11 March 2001, the second episode occurred from 12 to 16 April 2001. Yu utilized RSP data from Tap Mun and Tai Po stations in conjunction with trajectory analysis for the illustration of the long-range transport of air mass from the north before arriving at Hong Kong. Although PM_{2.5} quartz filters collected in the two episode periods were not sufficient for SEOC and WSOC determination, elemental analysis by XRF on Teflon filters revealed high silicon and calcium concentrations during these two events. High silicon and calcium values as observed in Figures 13 a to c may indicate one major source of PM during these events is originated from crustal sources and consistent with observation made by Yu (Appendix 9).

3.3.2 Ozone Episode

During the study period of the present 12-month PM speciation study, an ozone episode has been identified to occur between 14 and 19 September 2001. Typical characteristics of ozone episodes include stagnant air mass, low wind speed, strong solar radiation and high ozone concentrations at rural sites. For the ozone episode case from 14 to 19 September 2001, we specifically focused on 18 September 2001 when we captured diurnal carbonyls data to facilitate a better understanding of factors leading to an ozone episode. Preliminary findings of the September 2001 ozone episode has been reported before (Louie & Sin, 2002). Basically, in common with the previous ozone episode cases observed in autumn, the September 2001 ozone episode can be characterized with attributes such as light winds, independency of wind direction; and in the vicinity of the center of a large stagnating high pressure system. Other observations include the concentration of ozone peaks concurrently with those of formaldehyde and all other measured carbonyls in the afternoon at both Tsuen Wan (urban site) and Mong Kok

(roadside site) stations. Though ozone was not measured at Mong Kok, a peak carbonyl concentration was also found in the same period as that at Mong Kok.

3.4 TAP Monitoring in support of the 12-month PM_{2.5} study

TAP parameters including VOC, carbonyls, PAHs, dioxins & furans and total PCB are measured during the 12-month study period as additional information. The SOPs for TAP measurement are documented in TAP QA/QC manual (QA/QC Manual for Toxic Air Pollutants Monitoring Programme, HKEPD 2000). With the exception of total PCB, other TAP parameters follow the same concentration pattern as PM_{2.5}: roadside > urban > rural. Given in Figure 35a and b are plots of acetaldehyde and formaldehyde at CW and TW sites respectively. Figure 35 c shows dioxin distribution pattern at all sites: winter concentration > summer concentration. Presented in Figures 35 d to f are plots of selected VOC concentrations as represented by benzene, ethyl-benzene, toluene, and xylenes on a monthly basis. Again the seasonal and spatial patterns of TAPs are clear: winter > summer; roadside > urban > rural.

4 SUMMARY AND CONCLUSIONS

4.1 Chemical speciation information of PM_{2.5} in Hong Kong

- A total of 1080 filters were sampled for the present project; only 13 filters were invalidated; close to 99% of the sampled filters were valid for gravimetric and analytical determination.
- The annual averages of PM_{2.5} concentrations at TW, MK, and HT were found to be 34, 58, and 24 µg/m³ respectively. Mean mass concentrations of PM_{2.5} at Tsuen Wan (TW), Mong Kok (MK), and Hok Tsui (HT) for four seasons in Hong Kong were found to be in the range of 26 - 44, 51 - 69, and 15 - 32 µg/m³. One initial conclusion about the PM_{2.5} levels in Hong Kong can be drawn: roadside > urban > rural.
- Ammonium sulfate, organic carbon, and elemental carbon are the most abundant species found at all the sites. The annual mean concentration of ammonium sulfate, organics, and elemental carbon in the range of 8.6 to 9.5, 4.2 to 16.6, and 1.7 to 20.3 µg/m³ were measured at Mong Kok, Tsuen Wan, and Hok Tsui. At all sites, the geological material was found to represent only a small fraction of the total mass, ranging from only 0.6 to 2.3 µg/m³ or about 4% to 8% of the measured mass.
- The lack of variability of sulfate levels in PM_{2.5} found in all sites may be indicative of sulfur contribution from more regional sources. Secondary ammonium nitrate and ammonium sulfate seem to be similar among the sites, while the carbon becomes more elevated with proximity to sources.
- Seasonal pattern and spatial distribution of TAP parameters can be concluded: winter

> summer; roadside > urban > rural.

4.2 Solvent Extractable Organic Compounds

- Concentrations of SEOC in Hong Kong are in the range of 125 to 2060 ng/m³. Highest concentration of SEOC was found in winter at the roadside site and the lowest concentration at the rural site in summer. The UCM and FAs ranging from 32-71% and 23-56% of the total SEOC respectively are the most abundant components of SEOC. Other identified components include resolved AHs (5-21%), ROHs (0-5%) and PAHs (1-3%).

4.3 Water Soluble Organic Carbon

- 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 compounds (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 compounds mass. No discernible spatial variation is observed for these compounds, suggesting that they are most likely of secondary origin.

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