



Characteristics and source apportionment of PM₁ emissions at a roadside station

Y. Cheng^{a,b,c,*}, S.C. Zou^d, S.C. Lee^c, J.C. Chow^{a,b,e}, K.F. Ho^c, J.G. Watson^{a,b,e}, Y.M. Han^b, R.J. Zhang^f, F. Zhang^a, P.S. Yau^c, Y. Huang^c, Y. Bai^a, W.J. Wu^a

^a Department of Environmental Science and Technology, School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, No.28 Xianning West Road, Xi'an, Shaanxi, 710049, China

^b SKLLQG, Institute of Earth and Environment, CAS, Xi'an, Shaanxi, 710075, China

^c Department of Civil and Structural Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

^d School of Marine Sciences, Sun Yat-sen University, Guangzhou 510275, China

^e Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, USA

^f Key Laboratory of Regional Climate-Environment Research for Temperate East Asia, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China

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ABSTRACT

The mass concentrations of PM₁ (particles less than 1.0 μm in aerodynamic diameter), organic carbon (OC), elemental carbon (EC), water-soluble ions, and up to 25 elements were reported for 24 h aerosol samples collected every sixth day at a roadside sampling station in Hong Kong from October 2004 to September 2005. Annual average PM₁ mass concentration was $44.5 \pm 19.5 \mu\text{g m}^{-3}$. EC, OM (organic matter, $\text{OC} \times 1.2$), and SO_4^{2-} were the dominant components, accounting for ~36%, ~26%, and ~24% of PM₁, respectively. Other components, i.e., NO_3^- , NH_4^+ , geological material, trace elements and unidentified material, comprised the remaining ~14%. Annual average OC/EC ratio (0.6 ± 0.3) was low, indicating that primary vehicle exhaust was the major source of carbonaceous aerosols. The seasonal variations of pollutants were due to gas-particle partitioning processes or a change in air mass rather than secondary aerosol produced locally. Vehicle exhaust, secondary aerosols, and waste incinerator/biomass burning were dominant air pollution sources, accounting for ~38%, ~22% and ~16% of PM₁, respectively. Pollution episodes during summer (May–August) which were frequently accompanied by tropical storms or typhoons were dominated by vehicle emissions. During winter (November–February) pollution episodes coincided with northeasterly monsoons were characterized by secondary aerosols and incinerator/biomass burning emissions.

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1. Introduction

Adverse health effects of exposure to particles have been proven in numerous toxicological and epidemiological studies [1–5]. Fine particles, like PM₁ (particles with an aerodynamic diameter of less than 1.0 μm), are those most harmful to human beings, as they are able to penetrate into the human respiratory and circulation system, resulting in adverse health effects [4,6]. The mechanism of these adverse health effects is unclear; however, previous research indicates that toxic elements and compounds carried in fine particles may play an important role. About 70–80% of toxic trace

elements, like lead (Pb), cadmium (Cd), arsenic (As) and nickel (Ni), as well as Polycyclic Aromatic Hydrocarbon compounds (PAHs), were found in PM₁, with the majority of sulfur (S), vanadium (V), selenium (Se) and zinc (Zn) found in the submicron particle size range [7,8].

Fine particles, mainly arising from vehicle exhaust, comprised the majority of airborne total suspended particles (TSP) in the atmosphere of Hong Kong [9–12]. Lee et al. [11] found that PM₁ constituted ~70% of the PM_{2.5} mass at the Roadside Air Quality Monitoring Station on the campus of Hong Kong Polytechnic University (i.e., the PU Roadside Station). They suggested using PM₁ as an indicator for vehicular emissions at the PU Roadside Station due to less influence from non-vehicle sources [11]. The concentrations of the elements Cr, Fe, Co, Cu, As, and Ba at the roadside location were a factor of two higher than those measured at the background Hok Tsui (HT) station in Hong Kong [7]. In a roadside microenvironment, increasing particles counts were found when vehicles accelerate (e.g., after stopping at a

* Corresponding author at: Department of Environmental Science and Technology, School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, No.28 Xianning West Road, Xi'an, Shaanxi, 710049, China. Tel.: +86 29 83395078; fax: +86 29 83395078.

E-mail address: chengyan@mail.xjtu.edu.cn (Y. Cheng).

signal light or a bus stop), especially for diesel-fueled vehicles [13].

Previous studies [e.g., 11,14,15,16,17] have provided limited information on PM₁ in Hong Kong. For this study, 24 h sampling of PM₁ was conducted every sixth day at the PU Roadside Station from 8 October 2004 to 23 September 2005. Study objectives were to: (1) characterize the chemical composition and seasonal variation in speciated PM₁; (2) quantify the source contributions to PM₁ by the Positive Matrix Factorization (PMF) receptor model; and (3) investigate meteorological characteristics that may affect the occurrence and strength of each air pollution source.

2. Experimental method

2.1. Climate and sampling location

The climate in Hong Kong is sub-tropical, influenced by the Asian monsoons. The cooling of the great Asian land mass during winter and its heating during summer give rise to monsoonal winds on a very large scale, which leads to four seasons of unequal duration in Hong Kong [18]. The four seasons in this study are defined as prolonged summer (May–August) and winter (November–February), and transitional, short spring (March–April) and autumn (September–October), as listed in Table 1. An examination of the historical climatology records shows that meteorological characteristics during the study period did not deviate from the norm. Daily meteorological data was obtained from the Hong Kong Observatory.

PM₁ samples were collected at the PU Roadside Station (22.30° N, 114.17° E), located in a residential and commercial area near Victoria Harbour. The sampling site [11] is about 1–2 m away from the curb of Hong Chong Road, which is approximately 30 m wide with four lanes for each direction leading to the busiest cross-harbour tunnel in Hong Kong. During the sampling period, daily traffic flow remained at roughly 120,000 vehicles per day [19,20]. Traffic data were obtained from the toll data maintained for Victoria Harbour.

2.2. Sampling method

The 24 h PM₁ sampling was performed once every sixth day from 8 October 2004 to 23 September 2005 and forty valid sample sets were obtained. Approximately 5% of additional field blanks were collected for blank subtraction and error propagation. A URG-3000ABC sampler (URG corporation, Chapel Hill, USA) with one PM₁ inlet (Teflon® coated aluminum, URG corporation, Chapel Hill, USA), operated at 16.7 L/min, was used to collect samples. The sampling inlet was about 1.5 m above street level. The PM₁ sampler was equipped with two parallel channels containing 47 mm Teflon-membrane and quartz-fiber filters at the flow rate of 8.3 L/min for each channel. Both the Teflon-membrane and quartz-fiber filters were weighed twice before and after sampling, respectively, using a Sartorius Model MC5 Microbalance (Göttingen, Germany) with a sensitivity of ±1 µg in the 0–250 mg range. Before weighing, filters were equilibrated for 24 h in a desiccator at 20–30 °C and a relative humidity of 30–40%. Prior to sampling quartz-fiber filters were preheated in an electric furnace at 900 °C for 3 h to remove carbonaceous contaminants. Collected quartz fiber samples were stored in a refrigerator at about 4 °C to prevent the evaporation of volatile components prior to chemical analysis.

2.3. Chemical analyses

The Teflon-membrane filters were analysed for the presence of 51 elements (from Na to U) by X-ray fluorescence (XRF, Watson et al. [21]) at the Environmental Analysis Facility of the

Table 1
Summary of daily meteorological parameters and vehicle numbers in four seasons from October 2004 to September 2005.

Season	Temperature (°C)	RH (%)	Rainfall (mm)	Prevailing wind (°)	Wind speed (km hr ⁻¹)	Total bright sunshine (h)	Daily global solar radiation (MJ m ⁻²)	Mixing height ^a (m)	Daily diesel vehicle (#)	Daily total vehicle (#)
Spring	20.2 ± 4.2	81.6 ± 9.0	3 ± 4	67 ± 43	21 ± 10	4 ± 3	11 ± 6	1040 ± 631	39,214	123,130
Summer	28.0 ± 1.6	83.5 ± 6.3	35 ± 55	172 ± 74	22 ± 9	5 ± 4	14 ± 7	1116 ± 543	41,268	121,997
Autumn	26.6 ± 2.0	72.5 ± 11.4	13 ± 33	92 ± 83	23 ± 16	7 ± 6	15 ± 6	1053 ± 401	41,747	123,517
Winter	18.5 ± 3.6	76.0 ± 11.4	1 ± 2	55 ± 27	24 ± 9	5 ± 5	10 ± 3	1044 ± 538	38,066	122,690
Average	23.3 ± 5.2	78.9 ± 10.6	15 ± 46	102 ± 82	23 ± 10	5 ± 5	12 ± 7	1069 ± 536	39,955	122,580

^a Seven days with mixing height higher than 3000 were not counter here.

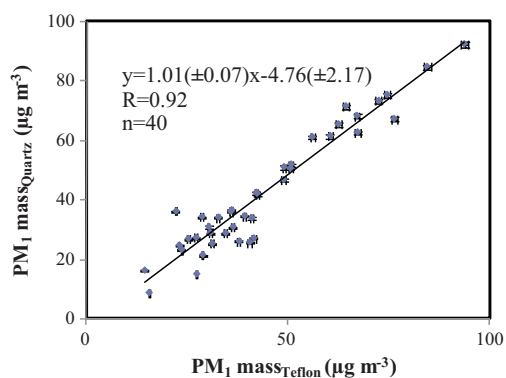


Fig. 1. PM_{10} gravimetric mass concentrations from Teflon-membrane and quartz-fiber filters at the PU Roadside Station from October 2004 to September 2005.

Desert Research Institute (Desert Research Institute, DRI, Reno, NV, USA). Half of the quartz-fiber filters were extracted with distilled-deionized water and the extracts were analysed for chloride (Cl^{-}), nitrate (NO_3^{-}), sulfate (SO_4^{2-}), water-soluble sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{2+}) and ammonium (NH_4^{+}) ions by ion chromatography (DIONEX, USA), following the methodology described by Chow and Watson [22], in the Air Laboratory of the Hong Kong Polytechnic University. OC and EC were measured on a 0.5 cm^2 quartz-fiber filter punch from the remaining half of the filters using a DRI Model 2001 carbon analyzer with a thermal-optical reflectance (TOR) method following the Inter-agency Monitoring of Protected Visual Environments (IMPROVE) protocol [23,24]. Field blanks were analysed for blank subtraction and error propagation.

Major mass constituents, including OC, EC, SO_4^{2-} , NO_3^{-} , NH_4^{+} , and elements (e.g., Al, Si, Ca, Fe, and Zn), were detected in almost every sample. Concentrations of only 25 elements were reported here because elements, such as Sc, Co, Ga, Se, Y, Nb, Mo, Pd, Ag, Cd, In, Sb, Cs, La, Ce, Sm, Eu, Tb, Hf, Ta, Wo, Ir, Au, Hg, Tl, and U, seldom showed concentrations higher than three times their respective minimum detectable limits (MDLs, [25]).

3. Results and discussion

3.1. Measurement validation

Because PM_{10} samples were acquired on two different substrates and chemical analyses were performed in different laboratories, consistency tests are needed as part of the quality assurance process. Fig. 1 shows the comparison of PM_{10} gravimetric mass measurements from the collocated Teflon-membrane and quartz-fiber filters. Good agreements (slope close to unity) and high correlation ($R=0.92$) demonstrated the consistency of sample and gravimetric analyses. Similar comparisons were also carried out by Engelbrecht et al. [26] in the USA and Louie et al. [14] in Hong Kong for $PM_{2.5}$ samples. Because quartz-fiber filters are known to have positive sampling artifacts due to absorption of gaseous organic compounds and water [27–31] and known to have a tendency to shred and fragment during sample handling, the following discussion refers to Teflon-membrane mass unless otherwise specified.

Regarding different chemical analysis methods, Fig. 2 shows reasonable agreement for SO_4^{2-} versus S ($R=0.97$), and K^{+} versus K ($R=0.98$), sampled on different sampling substrates. The ratio of SO_4^{2-} to S was 2.57 with a small intercept ($-0.05\text{ }\mu\text{g m}^{-3}$), indicating that more than $\sim 85\%$ of S was present as soluble SO_4^{2-} in the atmosphere and that both XRF and IC measurements were valid. The scatter plot of K^{+} and K also showed a slope of 0.92 and close to zero intercept ($-0.02\text{ }\mu\text{g m}^{-3}$) suggesting that over $\sim 90\%$ of total K

was present as soluble K^{+} in the atmosphere. These physical consistencies validate the effectiveness of the sampling and chemical analysis methods used in this study.

3.2. PM_{10} mass concentration and mass closure

The annual average PM_{10} mass concentration from October 2004 to September 2005 was $44.0 \pm 19.4\text{ }\mu\text{g m}^{-3}$ (Table 2). This level was higher than that measured at the urban Chung Shan site in Taiwan ($17.1, 13.1, 9.7\text{ }\mu\text{g m}^{-3}$ in spring, autumn and winter, respectively, [32]) and at the Virolahti background station in Finland (4.3 ± 3.8 and $3.8 \pm 3.6\text{ }\mu\text{g m}^{-3}$ in summer and winter, respectively, [33]), but much lower than that ($127.3 \pm 62.1\text{ }\mu\text{g m}^{-3}$) at an urban site in Xi'an, China [34]. Mass balance measurements of PM_{10} showed that EC, OM ($OM=OC \times 1.2$, [35]), and SO_4^{2-} were the major components of PM_{10} , accounting for $\sim 36\%$, $\sim 26\%$, and $\sim 24\%$ of the PM_{10} mass, respectively. Low abundances were found for NO_3^{-} ($\sim 5\%$), NH_4^{+} ($\sim 3\%$), geological material and trace elements ($\sim 3\%$), and unidentified material ($\sim 3\%$).

The statistical summary of PM_{10} mass concentration in Table 2 lists maximum PM_{10} mass concentration in winter ($52.9 \pm 20.1\text{ }\mu\text{g m}^{-3}$), followed by autumn ($48.7 \pm 24.8\text{ }\mu\text{g m}^{-3}$), spring ($41.3 \pm 7.5\text{ }\mu\text{g m}^{-3}$) and summer ($34.8 \pm 17.9\text{ }\mu\text{g m}^{-3}$). Hong Kong is located at south edge of East Asia and China. Monsoon winds exert a profound influence on the air quality of Hong Kong, as previously reported [11,14–16,36,37]. In the summer, prevailing southerly winds, with the resultant vector of 172° (Table 1), brought clean marine air masses to Hong Kong. In the autumn, winter, and spring, with the resultant vector of 71° (Table 1), prevailing northeasterly winds transported continental emissions from interior Asia to Hong Kong and the South China Sea. This explains the higher PM_{10} mass concentrations in winter, autumn, and spring compared to summer. Seasonal variation in mixing height, daily diesel vehicle numbers, and total vehicle numbers on the Hong Chong road (Table 1) are not significant factors that explain the seasonality of air pollution.

3.3. Carbonaceous aerosols

During the sampling period, PM_{10} OC ranged from 3.2 to $29.8\text{ }\mu\text{g m}^{-3}$ and EC ranged from 8.3 to $26.8\text{ }\mu\text{g m}^{-3}$. Annual average OC and EC were 9.6 ± 4.9 and $15.8 \pm 5.1\text{ }\mu\text{g m}^{-3}$, respectively. Compared to one of the most polluted inland cities (Xi'an) in China, average OC from this study was a factor of two lower than OC ($21.0\text{ }\mu\text{g m}^{-3}$) reported by Shen et al. [34], and average EC was three times higher than in Xi'an ($5.1\text{ }\mu\text{g m}^{-3}$), suggesting different source categories for carbonaceous aerosols between the two cities. The PU Roadside Station was dominated by fresh vehicle emissions, with a low average OC/EC ratio of 0.6 ± 0.3 , and Xi'an was dominated by coal combustion emissions, with a high OC/EC ratio of 4.4 [34]. It has been reported that fresh vehicle emissions accounted for more than 60% of OC at a typical roadside Mong Kok (MK) station in Hong Kong after examining detailed organic species in $PM_{2.5}$ using gas chromatography–mass spectrometry (GC/MS) method [38].

Average wintertime OC was $12.2 \pm 6.0\text{ }\mu\text{g m}^{-3}$ (Table 2), approximately 60% higher than summer. High OC concentrations at the PU Roadside Station in winter were not due to the nearby on-road primary vehicle exhaust because the daily percentage of diesel-fueled vehicles ($\sim 32\%$) and total traffic numbers on the Hong Chong road is consistent throughout the entire sampling period, as shown in Table 1. In addition, measurements of OC are sensitive to ambient and sampling conditions because gas-particle partitioning of OC are impacted by surrounding meteorological parameters. The seasonal data showed an inverse relationship between OC concentrations (Table 2) and temperature (Table 1) in line with the dynamic equi-

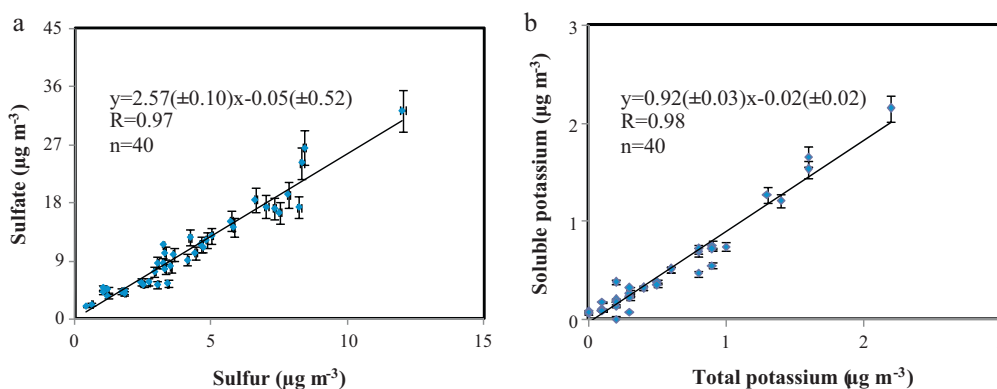


Fig. 2. Physical consistency tests of PM₁ measurements for (a) sulfate (SO₄²⁻) by ion chromatography on quartz-fiber filters versus total sulfur (S) by X-ray fluorescence (XRF) on Teflon-membrane filters; (b) soluble potassium (K⁺) versus total potassium (K).

librium between particle and gas phase OC, which supports high OC concentrations observed in winter. Except for primary sources, OC can be formed in the atmosphere as secondary aerosol that is typically enhanced when solar intensity is higher and daylight hours are longer. Table 1 shows that seasonal sunshine hours are highest in autumn when the OC/EC ratio is low indicating that it is not secondary aerosol produced locally but perhaps gas to particle partitioning processes or a change in air mass that is responsible for the seasonal changes. Pollutants transported from mainland China have been reported to increase the PM_{2.5} OC concentrations at the PU Roadside Station [11] and other ambient monitoring stations [14–16,36,37]. A previous study observed high OC concentrations (17.8 ± 10.2 µg m⁻³) and OC/EC ratios (2.9) in an upwind

area of Guangdong province [39], compared to those in Hong Kong. The seasonal EC concentrations showed highest value in summer (17.5 ± 5.8 µg m⁻³), followed by autumn (16.0 ± 8.0 µg m⁻³), winter (15.3 ± 3.8 µg m⁻³), and spring (12.2 ± 3.5 µg m⁻³). Good relationships between daily EC and wind speeds were found from November 2004 to April 2005 (winter and spring), with a correlation coefficient (*R*) of 0.72. EC decreased from 20.1 to 8.6 µg m⁻³ as northeasterly wind speeds increased from 8 to 39 km h⁻¹. In addition, the upwind area has less impact on EC levels at the PU Roadside Station when winter monsoons prevail because significantly lower EC (6.0 ± 3.2 µg m⁻³) has been reported over there [39]. Above evidence suggests that winter monsoons had a dispersive effect on EC concentrations.

Table 2

Statistical summary of 24 h PM₁ measurements at the PU Roadside Station from October 2004 to September 2005.

PM ₁ µg m ⁻³	Spring		Summer		Autumn		Winter		Total ^a	
	Average	SD ^b	Average	SD ^b	Average	SD ^b	Average	SD ^b	Average	SD ^b
Mass (Teflon)	41.3	7.5	34.8	17.9	48.7	24.8	52.9	20.1	44.0	19.4
Organic carbon (OC)	8.9	0.4	7.3	3.3	7.9	2.6	12.2	6.0	9.6	4.9
Elemental carbon (EC)	12.2	3.5	17.5	5.8	16.0	8.0	15.3	3.8	15.8	5.1
Chloride (Cl ⁻)	0.4	0.3	0.2	0.2	0.1	0.0	0.4	0.2	0.3	0.2
Nitrate (NO ₃ ⁻)	2.8	0.9	0.8	0.7	1.2	0.6	2.8	2.0	1.9	1.6
Sulfate (SO ₄ ²⁻)	10.0	5.3	6.7	5.0	15.6	14.5	13.9	6.0	10.7	7.1
Soluble sodium (Na ⁺)	1.2	0.1	1.3	0.2	1.1	0.1	1.3	0.2	1.3	0.2
Ammonium (NH ₄ ⁺)	3.0	1.1	1.4	1.3	3.4	2.7	3.3	1.4	2.5	1.6
Soluble potassium (K ⁺)	0.42	0.20	0.18	0.17	0.39	0.31	0.80	0.62	0.47	0.49
Sodium (Na)	0.43	0.17	0.39	0.36	0.69	0.43	0.53	0.21	0.48	0.29
Magnesium (Mg)	0.12	0.04	0.11	0.07	0.20	0.09	0.15	0.05	0.13	0.06
Aluminum (Al)	0.14	0.05	0.12	0.11	0.12	0.06	0.15	0.08	0.13	0.09
Silicon (Si)	0.18	0.09	0.14	0.17	0.17	0.09	0.30	0.17	0.21	0.17
Phosphorus (P)	0.18	0.08	0.12	0.10	0.29	0.23	0.21	0.08	0.18	0.11
Sulfur (S)	4.4	2.0	2.7	2.4	6.2	5.1	5.1	2.0	4.2	2.6
Chlorine (Cl)	0.41	0.60	0.10	0.03	0.12	0.10	0.19	0.15	0.21	0.26
Potassium (K)	0.50	0.26	0.20	0.21	0.44	0.34	0.89	0.58	0.54	0.51
Calcium (Ca)	0.06	0.02	0.08	0.11	0.06	0.02	0.08	0.05	0.07	0.07
Titanium (Ti)	0.0048	0.0032	0.0095	0.013	0.0058	0.0025	0.0085	0.0067	0.0082	0.0091
Vanadium (V)	0.015	0.011	0.017	0.019	0.016	0.006	0.016	0.018	0.016	0.017
Manganese (Mn)	0.018	0.006	0.015	0.013	0.016	0.005	0.029	0.021	0.021	0.017
Iron (Fe)	0.14	0.04	0.25	0.38	0.18	0.08	0.24	0.17	0.23	0.26
Nickel (Ni)	0.0048	0.0036	0.0054	0.0051	0.0035	0.0025	0.0055	0.0061	0.0052	0.0051
Copper (Cu)	0.011	0.002	0.012	0.013	0.014	0.004	0.016	0.008	0.013	0.009
Zinc (Zn)	0.11	0.06	0.18	0.21	0.24	0.11	0.26	0.18	0.21	0.18
Arsenic (As)	0.0078	0.0024	0.0050	0.0042	0.0147	0.0000	0.0150	0.0103	0.0127	0.0093
Bromine (Br)	0.011	0.005	0.007	0.005	0.005	0.001	0.017	0.013	0.012	0.010
Rubidium (Rb)	0.0031	0.0036	0.0017	0.0009	0.0039	0.0024	0.0070	0.0049	0.0045	0.0041
Strontium (Sr)	0.0051	0.0042	0.0041	0.0022	0.0043	0.0011	0.0046	0.0031	0.0045	0.0027
Zirconium (Zr)	0.0081	0.0011	0.0082	0.0049	0.0087	0.0036	0.0062	0.0043	0.0074	0.0043
Tin (Sn)	0.025	0.016	0.015	0.008	0.019	0.011	0.040	0.021	0.027	0.019
Antimony (Sb)	0.027	0.010	0.038	0.007	0.042	0.007	0.039	0.007	0.037	0.008
Barium (Ba)	0.029	0.023	0.025	0.023	0.044	0.026	0.025	0.011	0.027	0.019
Lead (Pb)	0.040	0.022	0.017	0.022	0.043	0.029	0.077	0.049	0.047	0.044

^a Total number of samples are equal to 40; ^b standard deviation.

In summer, a higher fraction of OC exists in the vapor phase as temperatures increase, which results in low particle OC concentration ($7.3 \pm 3.3 \mu\text{g m}^{-3}$) and low OC/EC ratio of 0.4 ± 0.1 . Among all potential sources (e.g., vehicle exhaust, cooking, and vegetative burning), vehicle exhaust is the most likely to produce such low OC/EC ratios [40]. Secondary organic aerosols were insignificant at the PU Roadside Station also in the summer because low OC/EC ratios and a moderate correlation between OC and total sunshine hours ($R=0.42$) and solar radiation ($R=0.06$) were observed. The summer daily OC and EC concentrations correlated well with prevailing wind directions, with correlation coefficients (R) of 0.76 and 0.84, respectively. Concentrations increased from 5.8 to $20.7 \mu\text{g m}^{-3}$ for OC, and from 9.4 to $27.1 \mu\text{g m}^{-3}$ for EC as the direction of the vector of prevailing winds changed from 50° to 300° . However, OC/EC ratios did not follow the changes in wind directions, with the minimum and maximum values of 0.31–0.62, respectively. The evidence above suggests the existence of primary sources southwest of the Hong Chong Road. Vehicle exhaust from the Victoria Harbour tunnel may contribute to observed carbonaceous aerosols, because the exit of the tunnel is about 800 m southwest of the PU Roadside Station in summer. In addition to vehicle exhaust from the tunnel, ship/container terminal emissions may contribute as well. Several container ports are distributed to the southwest of the PU sampling station, stretching for miles along the south coast of Kowloon Peninsula, Hong Kong. Elevated pollution levels around the Victoria Harbour area (near the sampling site) due to the influences of local vehicle exhaust and ship emissions have been reported by the Institute for the Environment of the Hong Kong University of Science and Technology (<http://envf.ust.hk>) and Civic Exchange (<http://www.civic-exchange.org/>).

3.4. Water-soluble ions and elements

Table 2 shows that SO_4^{2-} ($10.7 \pm 7.1 \mu\text{g m}^{-3}$) was by far the major PM_{10} ion, followed by NH_4^+ ($2.5 \pm 1.6 \mu\text{g m}^{-3}$), and NO_3^- ($1.9 \pm 1.6 \mu\text{g m}^{-3}$). Abundances of other ions were low: Na^+ ($1.3 \pm 0.2 \mu\text{g m}^{-3}$), K^+ ($0.47 \pm 0.49 \mu\text{g m}^{-3}$), and Cl^- ($0.3 \pm 0.2 \mu\text{g m}^{-3}$). Crustal elements (i.e., Fe, Si, Mg, Al, and Ca in decreasing concentrations) were low, in the range of 0.07–0.23 $\mu\text{g m}^{-3}$. Trace elements (i.e., Sb, Sn, Ba, Mn, V, Cu, As, Br, Ti, Zr, Ni, Rb, and Sr) were in the range of 0.0045 ± 0.0027 – $0.037 \pm 0.008 \mu\text{g m}^{-3}$, with the exception of Zn ($0.21 \pm 0.18 \mu\text{g m}^{-3}$) and P ($0.18 \pm 0.11 \mu\text{g m}^{-3}$). On average, water-soluble ions, crustal elements, and the remaining elements accounted for ~39%, 1.8%, and 0.6% of the PM_{10} mass, respectively.

Out of all water-soluble ions and elements, eight species, such as SO_4^{2-} , NH_4^+ , NO_3^- , Cl^- , K^+ , As, Br and Pb, exhibited significant seasonal differences at the 0.05 level using one-way analysis of variance (ANOVA) [41]. The concentrations of these pollutants were generally lowest during summer and highest during autumn and winter periods, as shown in Table 2. SO_4^{2-} and NH_4^+ had the highest concentrations in autumn, with average values of 15.6 ± 14.5 and $3.4 \pm 2.7 \mu\text{g m}^{-3}$, respectively.

Fine-mode SO_4^{2-} , NO_3^- , and NH_4^+ are secondary aerosols, arising from oxidation of gaseous precursors in air. Strong correlation ($R=0.96$) between SO_4^{2-} and NH_4^+ suggests their co-existence in the atmosphere. The relationships between NO_3^- and NH_4^+ were moderate ($R=0.61$). Comparisons between the calculated and observed NH_4^+ concentrations were conducted to evaluate the formation of ions. NH_4^+ concentration can be calculated based on the stoichiometric ratios of the major compounds (i.e., ammonium sulfate [(NH_4) $_2$ SO_4], ammonium bisulfate [NH_4HSO_4] and ammonium nitrate [NH_4NO_3]); assuming that NO_3^- is in the form of NH_4NO_3 and that SO_4^{2-} is in the form of either (NH_4) $_2$ SO_4 or NH_4HSO_4 . Fig. 3 shows the good correlation ($R=0.98$) between calculated and measured NH_4^+ concentrations. The slope was 1.7 when (NH_4) $_2$ SO_4 was

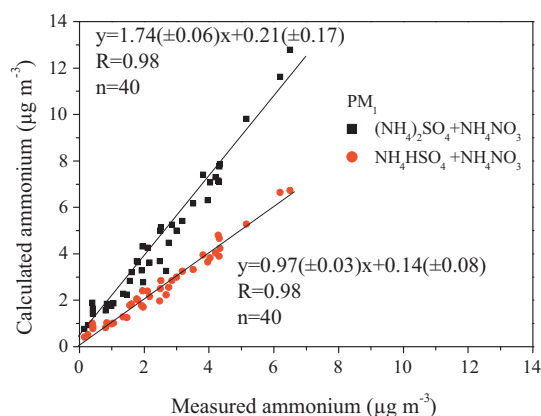


Fig. 3. Comparison between calculated and measured ammonium in PM_{10} (calculated $\text{NH}_4^+ = 0.38 \times [\text{SO}_4^{2-}] + 0.29 \times [\text{NO}_3^-]$) or NH_4HSO_4 (i.e., $\text{NH}_4^+ = 0.192 \times [\text{SO}_4^{2-}] + 0.29 \times [\text{NO}_3^-]$).

assumed and 1.0 when NH_4HSO_4 was assumed. This suggests that aerosol is acidic (i.e., not fully neutralized with available NH_4^+) and in the form of NH_4HSO_4 .

The anion and cation balance in Fig. 4 also shows high correlation ($R=0.98$). A deficiency of 11% in cations was found, especially at high loading concentrations, confirming the existence of acid aerosol. The seasonal anion-to-cation equivalent ratios (A/C) were 1.2 ± 0.04 , 1.0 ± 0.2 , 1.2 ± 0.3 and 1.2 ± 0.1 in spring, summer, autumn, and winter, respectively. Most samples had an A/C ratio higher than unity, especially during cold seasons. Increasing industrial activities in mainland China and prevailing northeasterly winds during winter may have contributed to the elevated SO_4^{2-} concentrations. Only ~27% of the PM_{10} samples, mostly from summer, gave A/C ratios less than unity.

Similar to those reported by Lin et al. [8], concentrations of crustal elements (i.e., Si, Al, Ca, Ti) were correlated with each other ($R>0.75$), while Fig. 2 shows that over 90% of K is in the form of K^+ , showing poor correlation with crustal elements. Abundant K in the form of K^+ suggests the influence of biomass burning and waste incinerator in the Macao Special Administrative Region (SAR) [14]. This is confirmed by good correlations ($R=0.8$) of K^+ with Rb and Pb.

The annual average Pb level ($47 \pm 44 \text{ ng m}^{-3}$) at the PU Roadside Station is three times lower than the annual USA standard of 150 ng m^{-3} . Annual average PM_{10} V ($16 \pm 17 \text{ ng m}^{-3}$), Mn ($21 \pm 17 \text{ ng m}^{-3}$), and Pb ($47 \pm 44 \text{ ng m}^{-3}$) are much lower than the World Health Organization [42] guideline values of 1, 0.15, and $0.5 \mu\text{g m}^{-3}$, respectively. Two carcinogenic substances, As

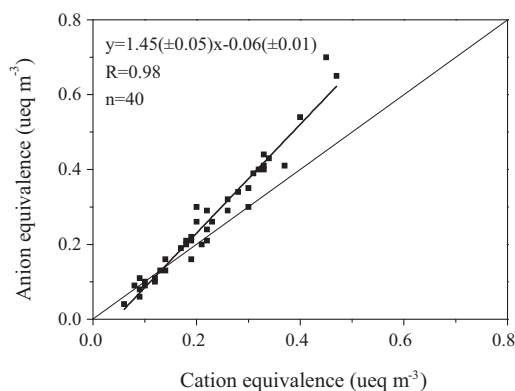


Fig. 4. Scatter plots of PM_{10} anion versus cation measurements from PM_{10} data. The anion equivalence was calculated from Cl^- , NO_3^- , SO_4^{2-} and the cation equivalence was calculated from Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} .

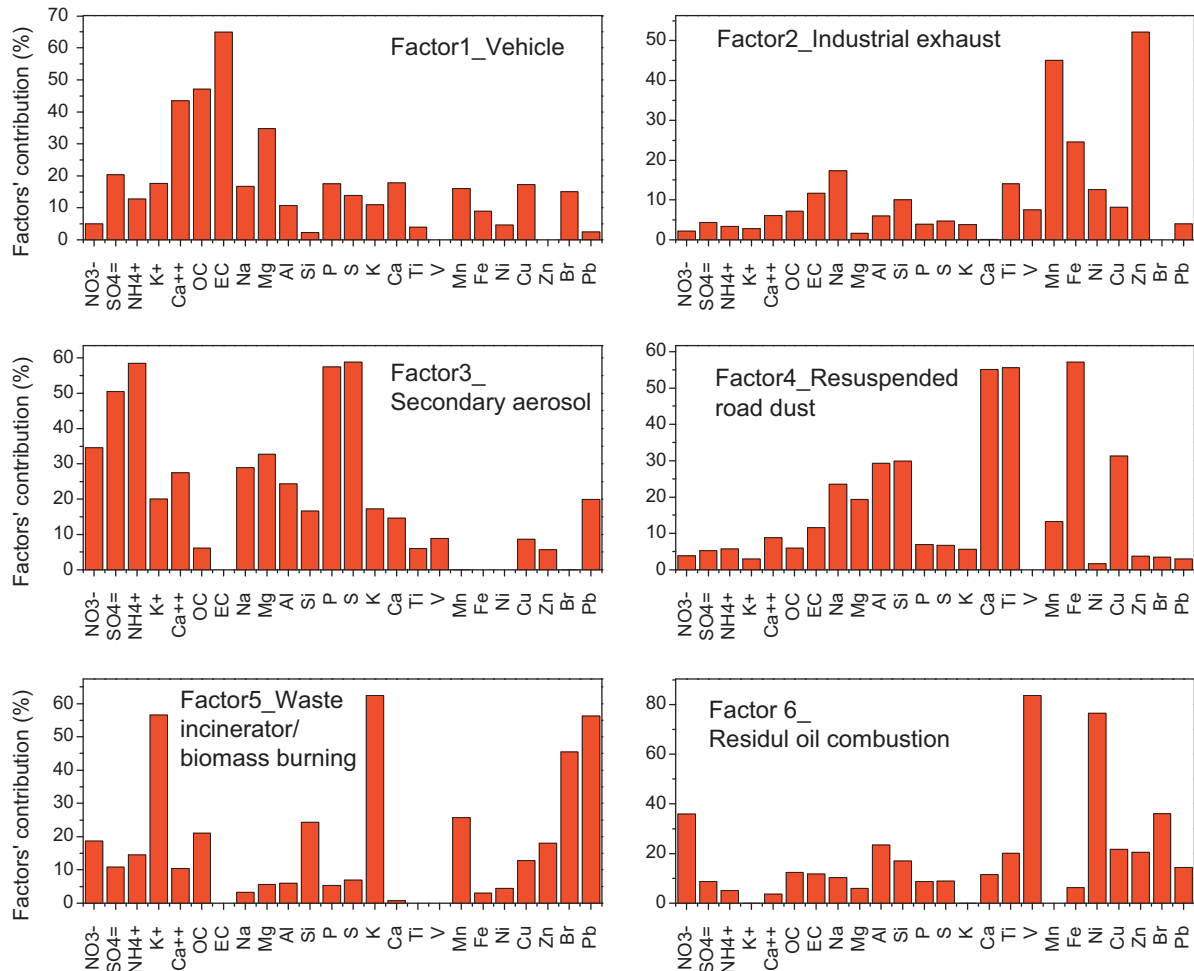


Fig. 5. Factor loadings obtained from positive matrix factorization (PMF) analysis of chemical constituents of PM₁.

(13 ± 9 ng m⁻³) and Ni (5 ± 5 ng m⁻³), and one toxic substance, Cu (13 ± 9 ng m⁻³), have concentrations lower than their California chronic exposure limits. Evidence indicates that all elements in PM₁ related to human health were lower than corresponding guideline values over the duration of four seasons at the PU Roadside Station.

3.5. Source apportionment by the PMF model

PMF has been shown to be a powerful tool for source identification [43,44] and has been used to assess PM_{2.5} and PM₁₀ source

contributions in the Arctic [45], Hong Kong [12,46], Thailand [47], Vermont [48], and cities in the USA [44,49–51]. For this study, measured concentration values and uncertainties (sampling and chemical analytical errors) were used as input data for the PMF3.0 model [52–54]. Species with a signal-to-noise ratio less than 0.2 were excluded from the analysis [54]. Finally, only 25 species were included in the PMF3.0, including mass, NO₃⁻, SO₄⁼, NH₄⁺, K⁺, Ca⁺⁺, OC, EC, Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br, and Pb. Forty samples were involved in the calculation.

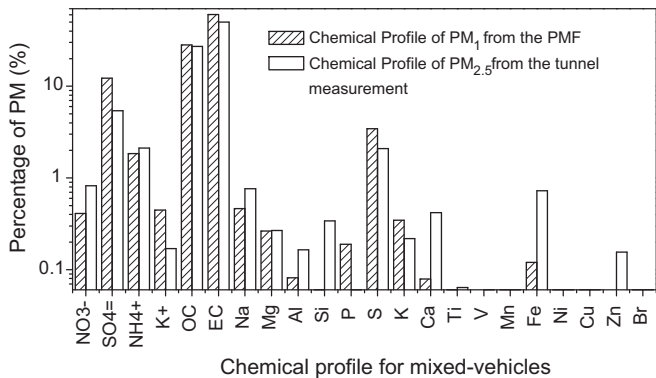


Fig. 6. Comparison of PMF-calculated and tunnel-measured vehicle chemical profiles in Hong Kong.

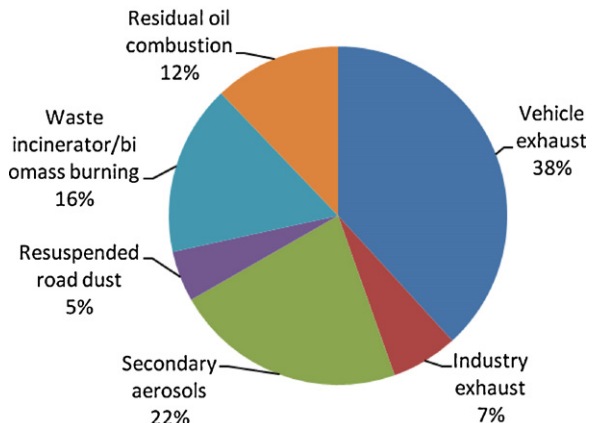


Fig. 7. Average source contributions of each factor to PM₁ mass.

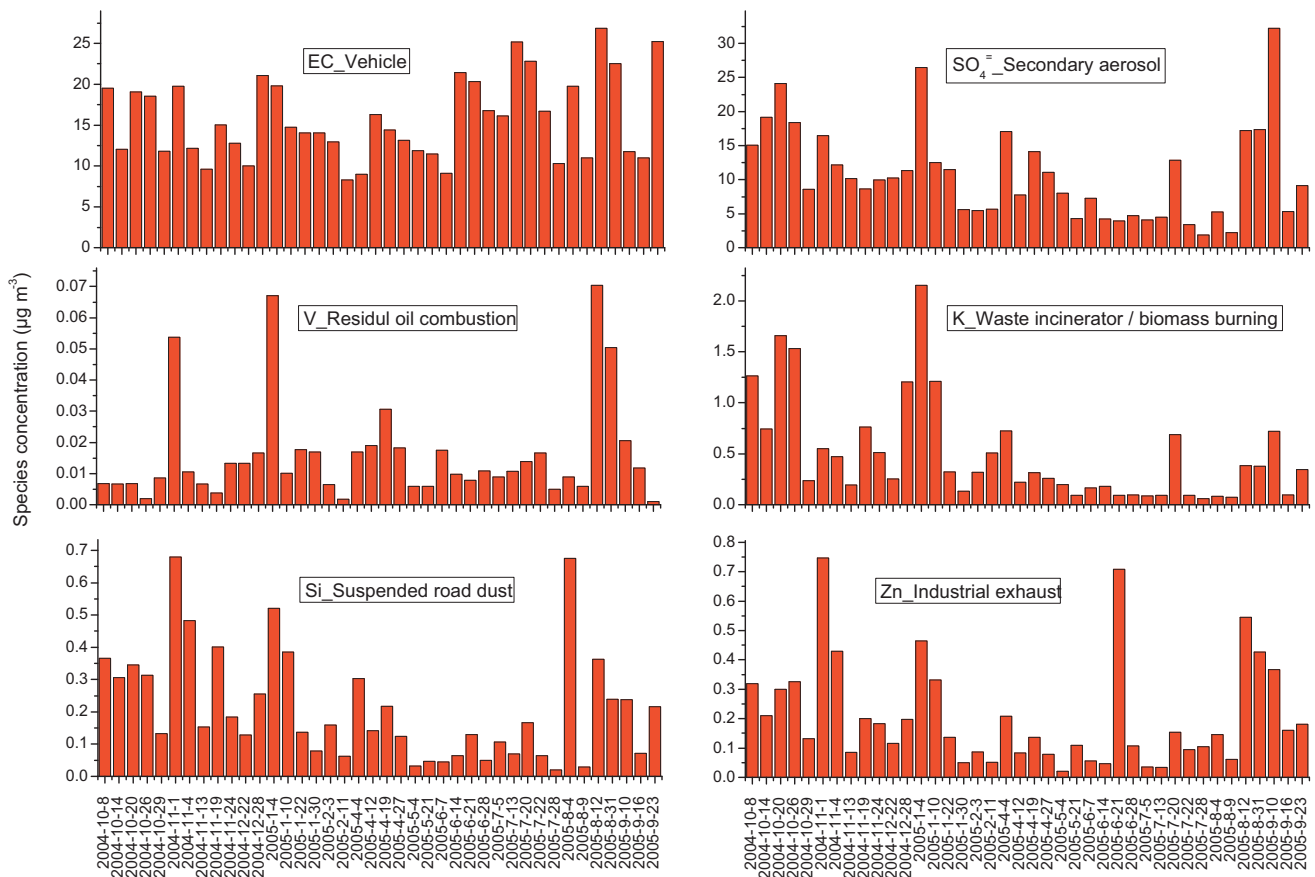


Fig. 8. Temporal patterns of marker species from the six source categories during the time period from October 2004 to September 2005.

Six factors were generated by the PMF model and the contributions of each factor are shown in Fig. 5. The first factor with high loading of OC, EC, and Ca^{2+} , are characteristic of vehicle exhaust [40,55–57] and lube oil additives [58], respectively. As shown in Fig. 6, the species abundances in this PMF-derived vehicle source profile are comparable to those measured in an urban tunnel in Hong Kong [55], especially for the major species (i.e., OC, EC, NO_3^- , SO_4^{2-} , NH_4^+ , Na, Mg, and K). PMF-derived vehicle source profiles underestimate crustal elements (i.e., Al, Si, Ca, Fe), which is reasonable because these elements mainly occur in $\text{PM}_{2.5}$ but not in PM_1 . The second factor, loaded with Mn and Zn, represents exhaust from industry [59,60]. The third factor is identified as secondary aerosols, based on the high abundances of NO_3^- , SO_4^{2-} , and NH_4^+ . The fourth factor, enriched with Al, Si, Ca, Ti, and Fe, is best explained as geological material or resuspended road dust [61,62]. The fifth factor with abundant K^+ , Br, and Pb, is indicative of waste incinerator/biomass burning emissions, as previously found by Louie et al. [14]. The sixth factor, loaded with V and Ni, is consistent with residual oil combustion, likely from ship emissions or utilities at container terminals [12,17].

Fig. 7 shows that vehicle exhaust is the largest contributor, accounting for $\sim 38\%$ of the PM_1 mass. This is consistent with sampling in a roadside vehicle exhaust-dominated environment. Secondary aerosols are the second largest contributor, accounting for $\sim 22\%$ of PM_1 . It has been shown through previous analyses that long-range transported secondary aerosols impact the air quality at the sampling site when the air mass has traveled over China before reaching Hong Kong. Waste incinerator/biomass burning and residual oil combustion account for $\sim 16\%$ and $\sim 12\%$ of PM_1 , respectively. Industrial exhaust and resuspended road dust account for $\sim 7\%$ and $\sim 5\%$ of PM_1 , respectively.

Marker species (i.e., EC, Zn, SO_4^{2-} , Si, K^+ , and V, respectively) were selected as representative components of their six respective source categories. Temporal patterns of marker species (Fig. 8) and meteorological characteristics on episode days (Table 3) were examined in order to identify essential meteorological parameters that may affect the occurrence and intensity of certain types of air pollution. The highest five concentrations for each marker species were considered to air pollution episodes, as shown in Table 3. Meteorological characteristics were obtained from the Hong Kong Observatory. The temporal patterns of SO_4^{2-} and K^+ suggest that secondary aerosols and waste incinerator/biomass burning frequently occurred in autumn, winter, and spring. The prevailing wind directions were 70° and 54° on the SO_4^{2-} and K^+ episode days, respectively. Moreover, elevated SO_4^{2-} , K^+ , and PM_1 concentrations often existed simultaneously. Vehicle exhaust episodes mainly occurred in summer, accompanied by typhoon or tropical storm events. Elevated PM_1 concentrations were often observed at the same time. The temporal variation in V showed weak seasonality for residual oil combustion sources. V and Ni correlated well with each other ($R=0.97$) and did not change with the changes in wind directions throughout the entire sampling periods. Therefore, ship emissions may also influence the PU Roadside Station as a regional pollution source. Wind direction was the most important meteorological parameter for industrial exhaust sources as they are stationary emitters. Resuspended road dust episodes predominantly occurred in winter, with less rainfall and dry northeasterly winds prevail.

Throughout the entire sampling period, air pollution on 4 January 2005 was the most serious, with all marker species showing elevated concentrations in the atmosphere, which could be explained by the extremely low mixing height of 477 m on that

Table 3
Summary of air pollution episodes (highest five concentrations of each marker species) from October 2004 to September 2005.

Episode day	PM ₁ mass	Vehicle exhaust	Secondary aerosols	Waste incinerator/bio moss burning	Resuspended road dust	Residual oil combustion	Industrial exhaust	Mixing height (m)	Air temperature (°C)	Relative humidity (%)	Rainfall (mm)	Prevailing wind direction (°)	Wind speed (km h ⁻¹)	Weather
	^a ^b	EC ~38%	SO ₄ ²⁻ ~22%	K ⁺ ~16%	Si ~5%	V ~12%	Zn ~7%							
8 October 2004	67.0			1.3				904	25.9	45%	0.0	10	17	Fine and dry
14 October 2004	55.9		19.2					1268	25.1	70%	0.1	90	36	Fine
20 October 2004	84.4		24.1	1.6				1022	24.8	74%	5.8	80	31	Haze
26 October 2004	67.1		18.4	1.6				967	25.5	58%	2.3	20	37	Fine
1 November 2004	62.4				0.7	0.054	0.7	663	23.1	70%	2.2	80	28	Some haze
4 November 2004	40.4				0.5		0.4	620	23.1	73%	0.0	80	29	Sunshine
19 November 2004	41.4				0.4			733	20.4	51%	0.0	90	21	Fine
4 January 2005	93.6		26.5	2.2	0.5	0.067	0.5	477	16.5	70%	1.2	70	26	Haze
10 January 2005	76.2			1.4				732	15.2	73%	0.0	90	24	Haze
19 April 2005	48.9					0.031		660	23.3	84%	4.7	70	19	Sunshine
21 June 2005	32.6						0.7	641	28.5	83%	9.7	230	22	Heavy rains and Thunderstorms
13 July 2005	40.9	25.2						842	29.8	75%	0.2	230	20	Sunny and hot
20 July 2005	64.2	22.8						573	28.7	81%	16.2	230	23	Sunny and hot; Thunderstorms
4 August 2005	25.1				0.7			836	28.5	82%	14.9	240	20	Sunny and hot; Thunderstorms
12 August 2005	74.5	26.8				0.070	0.5	738	28.3	83%	16.4	230	21	Haze; Thunderstorms
31 August 2005	60.4	22.5				0.050		728	29.4	76%	0.3	270	18	Fine
10 September 2005	72.4		32.2					898	28.1	78%	6.6	90	18	Haze
23 September 2005	50.6	25.2						838	28.6	67%	Trace	10	42	Hot and hazy
Annual average 44.0	15.7	10.7	0.5	0.2	0.016	0.2	1067	23.0		75%	10.8	87.8	23	Annual average 44.0

^a Marker species; ^b percentage of PM₁.

day. Overall, average concentrations of each marker species, except for EC, on episode days were around two to three times higher than the annual average values. The average concentration of EC was $24.5 \pm 1.8 \text{ ng m}^{-3}$ on episode days, approximately 1.6 times the annual average value. Meteorological data shows that low mixing heights (averaged at 786 m) occurred on all air pollution episode days and relative humidity ranged from 70 to 85%. Except for vehicle exhaust episodes, all air pollution episodes were associated with hazy, reduced visibility conditions, similar to those found in Beijing [63] and Guangzhou, China [64].

4. Conclusions

Twenty-four-hour PM_{10} samples were collected every sixth day at an urban roadside monitoring station in Hong Kong from October 2004 to September 2005. Concentrations of OC, EC, water-soluble ions, and up to 25 elements were reported. The seasonal average PM_{10} concentrations were 41.3 ± 7.5 , 34.8 ± 17.9 , 48.7 ± 24.8 , and $52.9 \pm 20.1 \text{ } \mu\text{g m}^{-3}$ for spring, summer, autumn, and winter, respectively. PM_{10} and major component species (e.g., OC, SO_4^{2-} , NO_3^- , NH_4^+ , etc.) showed distinct seasonal patterns with elevated concentrations typically in autumn, winter and spring, which were associated with northeasterly winds that transport from the continental Asian interior. Except for long-range transported regional pollutants, OC were impacted by gas-particle partitioning as well. EC was an exception with elevated concentrations in summer associated with primary emissions from local nearby tunnel and container ports. The low OC/EC ratio (<1) reflects that primary carbon emissions, rather than secondary organic aerosol, dominate this nearby roadside location.

Source apportionment of PM_{10} was carried out using a PMF model. Vehicle exhaust was the largest contributor to PM_{10} (~38%), followed by secondary aerosols (~22%), waste incinerator/biomass burning emissions (~16%), residual oil combustion (~12%), industrial exhaust (~7%) and resuspended road dust (~5%). Elevated PM_{10} mass concentrations were found when the sampling station was experiencing vehicle exhaust episodes in summer or secondary aerosols and waste incinerator/biomass burning emissions in winter. However, this was not the case when the station was impacted by residual oil combustion, industrial emissions, or resuspended road dust. Most air pollution episodes are associated with hazy, reduced visibility conditions, and low mixing heights (averaged at 786 m).

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