THE HONG KONG UNIVERSITY OF
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Final Report
for
Chemical Speciation of $PM_{2.5}$ Filter Samples

January 1 through December 31, 2014

(Tender Ref. 13-02772)

Prepared by:

Prof. Jian Zhen Yu
Dr. X. H. Hilda Huang
Dr. Ting Zhang
Ms. Wai Man Ng

Environmental Central Facility
The Hong Kong University of Science & Technology
Clear Water Bay, Kowloon, Hong Kong

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The Government of the Hong Kong Special Administrative Region

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1. Introduction

1.1 Background

The Environmental Protection Department of the Hong Kong Special Administration Region (HKEPD) put in force an updated Air Quality Objectives (AQOs) in January 2014. In the new AQOs, the concentration limit for 24-hour average $PM_{2.5}$ is set to be 75 µg/m^3 with 9 exceedance days allowed while the limit for annual average $PM_{2.5}$ is 35 µg/m^3.

The Environment Bureau (ENB) has been implementing a wide range of measures locally to reduce the air pollution. In November 2012, the Hong Kong Special Administrative Region (HKSAR) and Guangdong Provincial Governments also endorsed a new set of regional emission reduction targets for the next 10 to 15 years, strengthening the collaboration between Guangdong and Hong Kong to deal with the regional air pollution.

The on-going control measures aside, continuous monitoring of the air quality is necessary for the air pollution trend analysis. More specifically, the $PM_{2.5}$ chemical speciation studies would provide a better understanding on the nature and relative contributions of different emission sources that are responsible for the observed $PM_{2.5}$ levels in Hong Kong.

The HKEPD established a $PM_{2.5}$ chemical speciation network in 2000 and monitoring operations began in November, 2000. The HKEPD currently supports 7 sites as of the date of this report, which includes 4 collocated sites. The mass measurement data from the speciation network is used for identifying areas that meet or do not meet the new AQO criteria and supporting designation of an area as attainment or non-attainment. HKUST has been supporting HKEPD with the chemical speciation analysis of the $PM_{2.5}$ filter samples since 2011.

This report documents the $PM_{2.5}$ measurements and data validation for a twelve-month monitoring program from January to December 2014. The data were analyzed to characterize the composition and temporal and spatial variations of $PM_{2.5}$ concentrations in Hong Kong. Trends of $PM_{2.5}$ concentration and chemical composition were established by comparing the current study to the previous 12-month $PM_{2.5}$ studies since 2000. The monitoring data can further be used to explore the source contributions and investigate hypotheses regarding the formation of $PM_{2.5}$ episodes.

1.2 Project Objectives and Task Description

The Environmental Central Facility (ENVF) at the Hong Kong University of Science and Technology (HKUST) has been contracted by the Hong Kong Environmental Protection Department (HKEPD) in the analysis of $PM_{2.5}$ samples acquired over the course from January to December 2014. The objectives of this study were to:

- Determine the organic and inorganic composition of $PM_{2.5}$ and how it differs by season and proximity to different types of emission sources.
- Based on the ambient concentrations of certain tracer compounds, determine the contributions of different sources to $PM_{2.5}$ in Hong Kong.
- Investigate and understand the influences of meteorological/atmospheric conditions on $PM_{2.5}$ episodic events in Hong Kong.
- Establish inter-annual variability of $PM_{2.5}$ concentration and chemical composition in Hong Kong urban and rural areas.

The ENVF/HKUST team is responsible for:

- Receiving samples from the HKEPD and analyzing the filter samples for gravimetric mass and for an array of chemical constituents, including elements, soluble anions and cations, and carbonaceous material.
- Assembling validated sets of data from the analyses and preparing data files which will be entered into the HKEPD $PM_{2.5}$ speciation database.

1.3 Technical Approach

During the sampling period from January to December 2014, 24-hour $PM_{2.5}$ filter samples were acquired once every six days from the roadside-source-dominated Mong Kok (MK) Air Quality Monitoring Site (AQMS), the urban Central/Western (CW) and Tsuen Wan (TW) AQMSs, the new town Tung Chung (TC) and Yuen Long (YL) AQMSs, and the suburban Clear Water Bay (WB) Air Quality Research Site (AQRS) which is located on the campus of the Hong Kong University of Science and Technology. Starting from May 2014, a seventh site, Kwai Chung (KC) AQMS was added into the network. Three Partisol particle samplers (Rupprecht & Patachnick, Model 2025, Albany, NY) were used at MK, CW, WB, and TC sites while two Partisol samplers were placed at TW, YL, and KC sites to obtain $PM_{2.5}$ samples on both Teflon-membrane and quartz fiber 47-mm filters. All sampled Teflon-membrane and quartz fiber filters were analyzed for mass by gravimetric analysis by HKEPD's contractor and then subjected to a suite of chemical analyses, including 1) determination of elements for atomic number ranging from 11 (Sodium) to 92 (Uranium) using Energy-Dispersive X-Ray Fluorescence (ED-XRF) Spectroscopy; 2) determination of chloride, nitrate, sulfate, sodium, ammonium, and potassium using Ion Chromatography (IC); and 3) determination of organic carbon (OC), elemental carbon (EC), total carbon (TC) and individual thermal fractions for OC, EC, and pyrolyzed carbon on quartz fiber filters using Thermal Optical Transmittance (TOT) and Thermal Optical Reflectance (TOR) by both NIOSH and IMPROVE_A protocols.

2. Sampling Network

2.1 Ambient $PM_{2.5}$ Monitoring Network

24-hour $PM_{2.5}$ filter samples were taken at five AQMSs and one AQRS in Hong Kong once every six days from January to December 2014. Samplings in KC AQMS started in May 2014 and the sampling schedule was synchronized with those of the other six sites. The seven sampling sites are shown in Figure 1, representing roadside (MK), urban (CW, TW, and KC), new town (TC and YL), and suburban (WB) areas. The names, codes, locations, and descriptions of the individual sites are listed in Table 1.

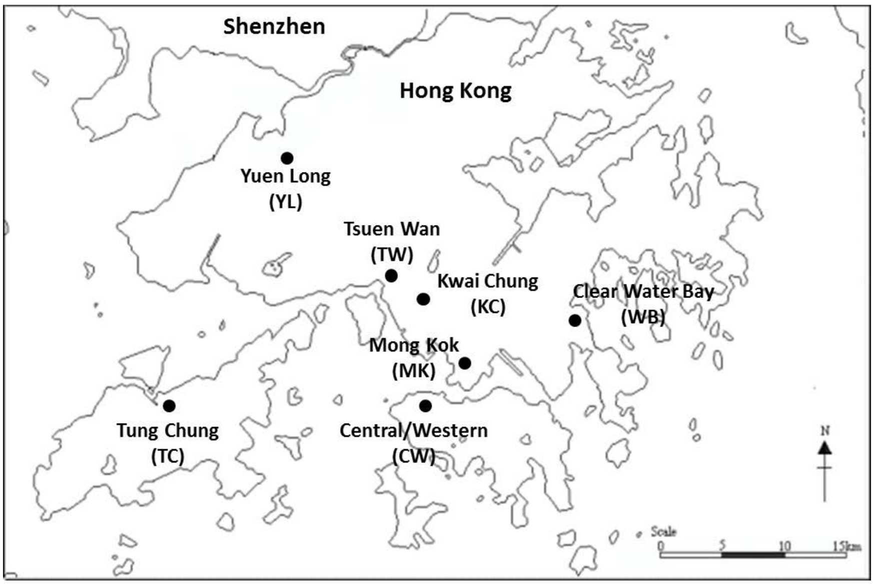


Figure 1. Monitoring sites in Hong Kong $PM_{2.5}$ speciation network.

Table 1. Descriptions of the monitoring sites.

Site Name	Site Code	Site Location	Site Description
Mong Kok	MK	Junction of Lai Chi Kok Road and Nathan Road, Kowloon	Urban roadside in mixed residential/commercial area with heavy traffic and surrounded by many tall buildings
Central/Western	CW	Rooftop of Sai Ying Pun Community Center, No. 2 High Street, Sai Ying Pun, Hong Kong	Urban, densely populated, residential site with mixed commercial development
Clear Water Bay	WB	Rooftop of a pump house next to Coastal Marine Lab, HKUST Campus, Clear Water Bay	Clean rural area with little residential and commercial development on the east coast of Sai Kung
Tung Chung	TC	Rooftop of Tung Chung Health Center, No. 6 Fu Tung Street, Lantau Island	Residential town, within 5 km southeast of HK International Airport
Tsuen Wan	TW	Rooftop of Princess Alexandra Community Center, 60 Tai Ho Road, New Territories	Urban, densely populated, residential site with mixed commercial and industrial developments. Located northwest of the MK site
Yuen Long	YL	Rooftop of Yuen Long District Branch Office Building, 269 Castle Peak Road, New Territories	Residential town, about 15 km southwest of Shenzhen
Kwai Chung	KC	Rooftop of the Kwai Chung Police Station, 999 Kwai Chung Road	Urban, densely populated residential site with mixed commercial and industrial developments, close to the Kwai Tsing Container Terminals

2.2 Ambient $PM_{2.5}$ Measurements

A total of 18 Partisol samplers were employed to obtain $PM_{2.5}$ samples around Hong Kong. The detailed arrangement of the samplers is described in Table 2.

Table 2. Arrangement of the Partisol samplers in the monitoring sites.

Location	No. of Samplers	Collocated Samples
MK AQMS	3	Teflon Filters
CW AQMS	3	Teflon Filters
WB AQRS	3	Quartz Fiber Filters
TC AQMS	3	Quartz Fiber Filters
TW AQMS	2	
YL AQMS	2	
KC AQMS	2	

Each Partisol sampler was equipped with an Andersen $PM_{2.5}$ inlet with Very Sharp Cut Cyclone (VSCC). The samplings were conducted at a flow rate of 16.7 L/min. At this flow rate, a nominal volume of approx. 24.0 m^3 of ambient air would be sampled over a 24-hour period. The Partisol samplers were configured to take either a Teflon-membrane filter or a quartz fiber filter. For this study, the following filters were chosen: 1) Whatman (Clifton, NJ, USA), $PM_{2.5}$ membrane, PTFE, 46.2 mm with support ring (#7592204); and 2) Pall Life Sciences (Ann Arbor, MI, USA), 2500QAT-UP, 47 mm, Tissuquartz^{TM} filters (#7202).

The Partisol samplers were operated and maintained by HKEPD's contractor, AECOM Asia Company Limited, throughout the study period. The ENVF/HKUST team was responsible for pre- and post-sampling procedures required for quality assurance and sample preservation. ENVF/HKUST team was also responsible for the gravimetric analysis on both filter types before and after sampling.

The collected Teflon-membrane filters were used for gravimetric analysis for $PM_{2.5}$ mass concentrations and elemental analysis (for more than 40 elements with atomic number ranging from 11 to 92) by X-Ray Fluorescence (XRF) [Watson et al., 1999]. The collected quartz fiber filters were analyzed for mass concentrations by gravimetry, for carbon contents by multiple thermal evolution methods, and for chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), water-soluble sodium (Na^+), ammonium (NH_4^+), and water-soluble potassium (K^+) by ion chromatography.

A major uncertainty in determining carbon concentrations lies in the differentiation of organic and elemental carbon during analysis. EC has been defined as the carbon that evolves after the detected optical signal attains the value it had prior to commencement of heating and the rest of the carbon is considered to be OC [Chow et al., 1993; Birch and Cary, 1996]. The split of OC and EC in the thermal analysis depends on several parameters including temperature setpoints, temperature ramping rates, residence time at each setpoint, combustion atmospheres, and optical signal used. Heating in an inert atmosphere causes certain OC to pyrolyze or char, inflating the EC in the sample. The extent of pyrolysis is dependent on thermal/temperature protocols. A laser is used to correct for pyrolitically-produced EC by monitoring changes in filter darkness during the thermal evolution process by detecting either filter transmittance (thermal/optical transmittance [TOT] method) or reflectance (thermal/optical reflectance [TOR] method). However, this introduces another problem related to inner/near-surface filter pyrolysis. It is found that pyrolysis occurs both within filter and on the filter surface. TOT method measures light transmittance which goes through the filter and is more likely influenced by the inner filter char while TOR method is more influenced by the charring of near-surface deposit.

In this study, two analytical protocols - National Institute of Occupational Safety and Health (NIOSH 5040) protocol coupled with TOT method for charring correction, and the Interagency Monitoring of Protected Visual Environments (IMPROVE_A) protocol coupled with TOR method for charring correction are employed to analyze the quartz fiber filters. Table 3 shows the temperature programs of the NIOSH and IMPROVE_A protocols. Results obtained with the two protocols are compared and evaluated in Section 3.3.4.

Table 3. Temperature programs of the NIOSH and IMPROVE_A protocols.

Carrier gas	**Carbon fraction**	**NIOSH_TOT temp, time**	**IMPROVE_A_TOR temp, time**
He purge		25°C, 10 s	25°C, 10 s
He-1	OC1	310°C, 80 s	140°C, 150-580 s
He-2	OC2	475°C, 60 s	280°C, 150-580 s
He-3	OC3	615°C, 60 s	480°C, 150-580 s
He-4	OC4	870°C, 90 s	580°C, 150-580 s
He-5		Cool oven	-
O_2 / He-1	EC1	550°C, 45 s	580°C, 150-580 s
O_2 / He-2	EC2	625°C, 45 s	740°C, 150-580 s
O_2 / He-3	EC3	700°C, 45 s	840°C, 150-580 s
O_2 / He-4	EC4	775°C, 45 s	
O_2 / He-5	EC5	850°C, 45 s	
O_2 / He-6	EC6	870°C, 45 s	

2.3 Sample Delivery and Filter Conditions

A total of 1164 filter samples including 582 Teflon filters and 582 quartz fiber filters were received. The sampling dates on which the samples were collected were summarized in Table 4. In 2014, there were 60 sampling events at MK, CW, WB, TC, TW, and YL sites while 41 sampling events at KC site.

Table 4. Valid sampling dates for the PM$_{2.5}$ samples in 2014 (Tender Ref. 13-02772).

January	February	March	April	May	June
140107 w/BLK 140113 140119 140125 140131	140206 140212 140224 140227 w/BLK	140302 140308 140314 140320 140326	140401 140407 140413 140419 140425	140501 w/BLK 140507 140513 140519 140525 140531	140606 140612 140618 140624 140630 w/BLK
July	**August**	**September**	**October**	**November**	**December**
140706 140712 140718 140724	140805 140807 140811 140817 140823 140829 w/ BLK	140904 140910 140916 140922 140928	141004 141010 141016 141022 141028 w/BLK	141103 141115 141118 141121 141127	141203 141209 141215 141221 141227 w/BLK

During the Level I data validation, 8 filter samples were identified to be invalid. The corresponding sample IDs, filter IDs, and a brief account for invalidating these samples are provided in Table 5.

Table 5. List of invalid filter samples in 2014 (Tender Ref. 13-02772).

Sample ID	Filter ID	PM$_{2.5}$ Mass (Teflon), μg/m^3	PM$_{2.5}$ Mass (Quartz), μg/m^3	Remark
MK140425SF01Q	Q0020086	46.79/43.04	-	Power failure
MK140501SF01Q	Q0020094	32.88/32.67	-	Power failure
MK140507SF01Q	Q0020112	32.75/30.92	-	Power failure
WB140513SF01Q	Q0020123	8.67	-/8.42	Power failure
TC140817SF02T	T0010373	-	10.75/10.29	Program error
TW140519SF02T	T0010221	-	12.79	Pinhole found on the filter
YL141215SF01Q	Q0020497	70.67	-	Power failure
KC140805SF02T	T0010349	-	21.92	Scratch found on the filter

*For MK and CW sites, the PM mass data obtained from Teflon samples were presented as mass from channel 2 (SF02T) / mass from channel 3 (PF03T); for WB and TC sites, the PM mass data obtained from quartz fiber samples were presented as mass from channel 1 (SF01Q) / mass from channel 3 (PF03Q).

For the 3 sampling dates on which the channel 1 quartz fiber filter samples were identified invalid at MK site, the chemical information was incomplete since only one quartz fiber filter sample was collected at this site in every sampling event.

For the WB filter samples collected on May 13, 2014, invalid flag was put onto one of the quartz fiber filters while the collocated quartz fiber filter sample was valid. Therefore, it was still able to obtain complete chemical information for WB on that day.

For the TC filter samples collected on August 17, 2014, since there was only one Teflon filter collected at this site and TC140817SF02T was flagged as invalid due to program error, the chemical information was incomplete for TC on that day.

For TW140519, YL141215, and KC140805, since there were only one Teflon filter and one quartz fiber filters collected in each sampling event, any invalid samples would lead to incomplete chemical information for the site.

3. Database and Data Validation

3.1 Data File Preparation

An electronic database for the analytical results is established for Hong Kong $PM_{2.5}$ data archive. Detailed data processing and data validation are documented in Section 3.3. The data are available on Compact Disc in the format of Microsoft Excel spreadsheets for convenient distribution to data users. The contents of the final data files are summarized in Table 6.

Table 6. Summary of data files for the $PM_{2.5}$ study (EPD Tender Ref. 13-02772) in Hong Kong.

Category	Database File	File Description
I. DATABASE DOCUMENTATION		
	13-02772_ID.xls	Defines the field sample names, measurement units, and formats used in the database file
II. MASS AND CHEMICAL DATA		
	13-02772_PM2.5.xls	Contains $PM_{2.5}$ mass data and chemical data for samples collected by Partisol samplers at seven sites once every six days in 2014
III. DATABASE VALIDATION		
	13-02772_FLAG.xls	Contains both field sampling and chemical analysis data validation flags

3.2 Measurement and Analytical Specifications

The measurement/analysis methods are described in Section 2 and every measurement consists of 1) a value; 2) a precision (uncertainty), and 3) a validity statement. The values are obtained by different analysis methods. The precisions are estimated through standard testing, blank analysis, and replicate analysis. The validity of each measurement is indicated by appropriate flagging in the data base, while the validity of chemical analysis results are evaluated by data validations described in Section 3.3.

A total of 60 sets of ambient $PM_{2.5}$ samples and 7 sets of field blanks were received during this study. Collocated sampling was conducted at 4 out of 7 sites and the collocated samples were used for data validation purpose. Of the 1042 $PM_{2.5}$ filter samples received, 1034 filter samples are considered valid after Level I data validation. Therefore, a total of 1156 filters (1034 $PM_{2.5}$ samples and 122 field blanks) were submitted for comprehensive chemical analyses.

3.2.1 Precision Calculations and Error Propagation

Measurement precisions are propagated from precisions of volumetric measurements, chemical composition measurements, and field blank variability using the methods of Bevington [1969] and Watson et al. [2001]. The following equations are used to calculate the prevision associated with filter-based measurements:

$$C_i = \frac{M_i - B_i}{V} \qquad (1)$$

$$V = Q \times T \qquad (2)$$

$$B_i = \frac{1}{n}\sum_{o=1}^{n} B_{io} \qquad \mathit{for}\ B_i > \sigma_{B_i} \qquad (3)$$

$$B_i = 0 \qquad \mathit{for}\ B_i < \sigma_{B_i} \qquad (4)$$

$$\sigma_{B_i} = STD_{B_i} = \left[\frac{i}{n-1}\sum_{o=1}^{n}\left(B_{io} - B_i\right)^2\right]^{\frac{1}{2}} \qquad \mathit{for}\ STD_{B_i} > SIG_{B_i} \qquad (5)$$

$$\sigma_{B_i} = SIG_{B_i} = \left[\frac{i}{n}\sum_{o=1}^{n}\left(\sigma_{B_{io}}\right)^2\right]^{\frac{1}{2}} \qquad \mathit{for}\ STD_{B_i} \leq SIG_{B_I} \qquad (6)$$

$$\sigma_{C_i} = \left[\frac{\sigma_{M_i}^2 + \sigma_{B_i}^2}{V^2} + \frac{\sigma_V^2\left(M_i - B_i\right)^2}{V^4}\right]^{\frac{1}{2}} \qquad (7)$$

$$\sigma_{RMSi} = \left(\frac{1}{n}\sum_{o=1}^{n}\sigma_{C_i}^2\right)^{\frac{1}{2}} \qquad (8)$$

$$\frac{\sigma_V}{V} = 0.05 \qquad (9)$$

Where:

B_i = average amount of species i on field blanks

B_{io} = the amount of species i found on field blank o

C_i = the ambient concentration of species i

Q = flow rate throughout sampling period

M_i = amount of species i on the substrate

N = total number of samples in the sum

SIG_{Bi} = the root mean square error (RMSE), the square root of the averaged sum of the squared σ_{Bio}

STD_{Bio} = standard deviation of the blank

σ_{Bi} = blank precision for species i

σ_{Bio} = 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_{RMSi} = root mean square precision for species i

σ_{V} = precision of sample volume

T = sample duration

V = volume of air sampled

The uncertainty of the measured value and the average uncertainty of the field blanks for each species are used to propagate the overall precision for each blank subtracted concentration value. The final value is propagated by taking the square root of the sum of the squares of the calculated uncertainty and the average field blank uncertainty for each measurement.

3.2.2 Analytical Specifications

The concentrations of field blanks collected during the study are summarized in Table 7 in the unit of µg/filter.

Blank precisions (σ_{Bi}) are defined as the higher value of the standard deviation of the blank measurements, STD_{Bi}, or the square root of the averaged squared uncertainties of the blank concentrations, SIG_{Bi}. If the average blank for a species was less than its precision, the blank was set to zero (Eqn 4).

The precisions (σ_{Mi}) were determined from duplicate analysis of samples. When duplicate sample analysis is made, the range of results, R, is nearly as efficient as the standard deviation since two measures differ by a constant (1.128s = R where s represents the precision).

Table 7. Field blank concentrations of $PM_{2.5}$ samples collected at MK, CW, WB, TC, TW, YL, and KC sites during the study period in Hong Kong.

	Amounts in µg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD_{Bi})**	**Root Mean Squared Blank Precision (SIG_{Bi})**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B_i)**
Na^+	61	1.680	0.813	1.680	0.069	0.000
NH_4^+	61	1.838	0.349	1.838	-0.454	0.000
K^+	61	0.491	1.360	1.360	-0.174	0.000
Cl^-	61	1.467	1.192	1.467	2.656	2.656
NO_3^-	61	4.006	2.974	4.006	6.808	6.808
SO_4^{2-}	61	8.936	2.721	8.936	8.177	0.000
OC1_TOR	61	1.058	1.874	1.874	5.045	5.045
OC2_TOR	61	1.045	2.981	2.981	5.922	5.922
OC3_TOR	61	2.039	3.801	3.801	8.105	8.105
OC4_TOR	61	0.791	2.105	2.105	2.204	2.204
OC_TOR	61	4.464	10.282	10.282	19.757	19.757
OC_TOT	61	7.616	3.463	7.616	20.935	20.935
PyC_TOR	61	3.233	1.610	3.233	-1.519	0.000
PyC_TOT	61	0.601	2.419	2.419	0.454	0.000
EC1_TOR	61	0.846	2.878	2.878	1.070	0.000
EC2_TOR	61	0.713	1.924	1.924	2.356	2.356
EC3_TOR	61	0.934	1.856	1.856	2.092	2.092
EC_TOR	61	4.110	5.220	5.220	7.037	7.037
EC_TOT	61	0.085	2.396	2.396	-0.010	0.000
TC_TOR	61	5.350	15.212	15.212	26.793	26.793
Na	61	0.1200	0.4435	0.4435	0.1287	0.0000
Mg	61	0.1893	1.6322	1.6322	0.3339	0.0000
Al	61	0.1197	0.6810	0.6810	0.1596	0.0000
Si	61	0.1648	0.3867	0.3867	-0.0144	0.0000
P	61	0.0231	0.0951	0.0951	0.0584	0.0000
S	61	0.0077	0.0554	0.0554	0.0013	0.0000
Cl	61	0.0340	0.0898	0.0898	0.0200	0.0000
K	61	0.0209	0.0428	0.0428	0.0128	0.0000
Ca	61	0.0575	0.0735	0.0735	-0.0185	0.0000

	Amounts in µg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD$_{Bi}$)**	**Root Mean Squared Blank Precision (SIG$_{Bi}$)**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B$_i$)**
Sc	61	0.0520	0.4728	0.4728	0.0214	0.0000
Ti	61	0.0155	0.0332	0.0332	0.0095	0.0000
V	61	0.0048	0.0138	0.0138	0.0039	0.0000
Cr	61	0.0186	0.0280	0.0280	0.0193	0.0000
Mn	61	0.0382	0.0992	0.0992	0.0342	0.0000
Fe	61	0.0484	0.1582	0.1582	0.0828	0.0000
Co	61	0.0075	0.0183	0.0183	0.0069	0.0000
Ni	61	0.0304	0.0268	0.0304	0.0028	0.0000
Cu	61	0.0200	0.0465	0.0465	-0.0022	0.0000
Zn	61	0.0200	0.0915	0.0915	0.0055	0.0000
Ga	61	0.0241	0.0858	0.0858	0.0263	0.0000
Ge	61	0.0127	0.0657	0.0657	0.0066	0.0000
As	61	0.0000	0.0557	0.0557	0.0000	0.0000
Se	61	0.0000	0.0490	0.0490	0.0000	0.0000
Br	61	0.0142	0.0355	0.0355	0.0125	0.0000
Rb	61	0.0116	0.0528	0.0528	-0.0143	0.0000
Sr	61	0.0155	0.0234	0.0234	-0.0159	0.0000
Y	61	0.0110	0.0738	0.0738	0.0005	0.0000
Zr	61	0.0301	0.0944	0.0944	0.0421	0.0000
Nb	61	0.0274	0.0725	0.0725	0.0422	0.0000
Mo	61	0.0283	0.1336	0.1336	0.0392	0.0000
Rh	61	0.0488	0.1967	0.1967	0.0285	0.0000
Pd	61	0.0602	0.1296	0.1296	0.0452	0.0000
Ag	61	0.0427	0.1050	0.1050	-0.0216	0.0000
Cd	61	0.0365	0.1716	0.1716	0.0065	0.0000
In	61	0.0558	0.1925	0.1925	0.0002	0.0000
Sn	61	0.0767	0.1430	0.1430	-0.0530	0.0000
Sb	61	0.0605	0.2740	0.2740	0.0157	0.0000
Te	61	0.0938	0.3344	0.3344	-0.0015	0.0000
I	61	0.1192	1.4097	1.4097	-0.0460	0.0000
Cs	61	0.2262	2.2346	2.2346	0.5429	0.0000
Ba	61	0.2311	2.0525	2.0525	0.1795	0.0000

	Amounts in µg/47-mm filter					
Species	**Total No. of Blanks**	**Field Blank Std. Dev. (STD_{Bi})**	**Root Mean Squared Blank Precision (SIG_{Bi})**	**Blank Precision (σ_{Bi})**	**Average Field Blank**	**Blank Subtracted (B_i)**
La	61	0.2754	0.3378	0.3378	0.3095	0.0000
Ce	61	0.0216	0.0691	0.0691	0.0218	0.0000
Sm	61	0.0315	0.1229	0.1229	-0.0207	0.0000
Eu	61	0.0637	0.0869	0.0869	0.0416	0.0000
Tb	61	0.0301	0.5524	0.5524	0.0031	0.0000
Hf	61	0.0985	0.3049	0.3049	0.1291	0.0000
Ta	61	0.0572	0.5725	0.5725	0.0270	0.0000
W	61	0.1862	0.0910	0.1862	-0.0763	0.0000
Ir	61	0.0335	0.0456	0.0456	-0.0499	0.0000
Au	61	0.0315	0.0681	0.0681	0.0171	0.0000
Hg	61	0.0068	0.0768	0.0768	0.0008	0.0000
Tl	61	0.0266	0.1166	0.1166	0.0414	0.0000
Pb	61	0.0354	0.1444	0.1444	0.0452	0.0000
U	61	0.0459	0.0091	0.0459	-0.0001	0.0000

The analytical specifications for the 24-hour $PM_{2.5}$ measurements obtained during the study are summarized in Table 8. Limits of detection (LOD) and limits of quantitation (LOQ) are given. The LOD of an analyte may be described as that concentration which gives an instrument signal significantly different from the "blank" or "background" signal. In this study LOD is defined as the concentration at which instrument response equals three times the standard deviation of the concentrations of low level standards. As a further limit, the LOQ is regarded as the lower limit for precise quantitative measurements and is defined as a concentration corresponding to ten times the standard deviation of the concentrations of low level standards. The LOQs should always be equal to or larger than the analytical LODs and it was the case for all the chemical species listed in Table 8. Both the LODs and LOQs are in the unit of µg/filter assuming the effective sampling area of the 47-mm filter is 11.98 cm^2.

Table 8. Analytical specifications of 24-hour $PM_{2.5}$ measurements at MK, CW, WB, TC, TW, YL, and KC sites during the study period in Hong Kong.

Species	**Analytical Method**	**LOD ($\mu g/m^3$)**	**LOQ ($\mu g/m^3$)**	**No. of valid Values**	**No. > LOD**	**% > LOD**	**No. > LOQ**	**% > LOQ**
Na^+	IC	0.008	0.028	513	513	100%	513	100%
NH_4^+	IC	0.003	0.011	513	510	99%	510	99%
K^+	IC	0.014	0.047	513	450	88%	450	88%
Cl^-	IC	0.012	0.041	513	380	74%	332	65%
NO_3^-	IC	0.030	0.101	513	481	94%	448	87%
SO_4^{2-}	IC	0.027	0.088	513	513	100%	513	100%
OC1_TOR	TOR	0.035	0.118	513	486	95%	486	95%
OC2_TOR	TOR	0.058	0.195	513	513	100%	513	100%
OC3_TOR	TOR	0.074	0.246	513	512	100%	512	100%
OC4_TOR	TOR	0.043	0.145	513	513	100%	513	100%
OC_TOR	TOR	0.202	0.674	513	513	100%	513	100%
OC_TOT	TOT	0.167	0.556	513	513	100%	513	100%
PyC_TOR	TOR	0.036	0.122	513	468	91%	462	90%
PyC_TOT	TOT	0.055	0.185	513	485	95%	421	82%
EC1_TOR	TOR	0.061	0.205	513	513	100%	511	100%
EC2_TOR	TOR	0.039	0.131	513	502	98%	496	97%
EC3_TOR	TOR	0.038	0.127	513	379	74%	164	32%
EC_TOR	TOR	0.106	0.353	513	513	100%	510	99%
EC_TOT	TOT	0.002	0.008	513	510	99%	510	99%
TC	TOR	0.302	1.006	513	513	100%	513	100%
Na	XRF	0.0109	0.0362	517	516	100%	516	100%
Mg	XRF	0.0554	0.1846	517	516	100%	277	54%
Al	XRF	0.0258	0.0861	517	517	100%	407	79%
Si	XRF	0.0162	0.0539	517	507	98%	449	87%
P	XRF	0.0032	0.0105	517	509	98%	350	68%
S	XRF	0.0023	0.0076	517	517	100%	517	100%
Cl	XRF	0.0036	0.0120	517	515	100%	429	83%
K	XRF	0.0017	0.0056	517	517	100%	517	100%
Ca	XRF	0.0032	0.0106	517	517	100%	516	100%
Sc	XRF	0.0195	0.0649	517	0	0%	0	0%
Ti	XRF	0.0013	0.0044	517	497	96%	402	78%

Species	**Analytical Method**	**LOD (µg/m^3)**	**LOQ (µg/m^3)**	**No. of valid Values**	**No. > LOD**	**% > LOD**	**No. > LOQ**	**% > LOQ**
V	XRF	0.0006	0.0018	517	517	100%	511	99%
Cr	XRF	0.0011	0.0036	517	330	64%	111	21%
Mn	XRF	0.0038	0.0128	517	455	88%	240	46%
Fe	XRF	0.0059	0.0198	517	517	100%	513	99%
Co	XRF	0.0007	0.0024	517	163	32%	4	1%
Ni	XRF	0.0011	0.0036	517	498	96%	300	58%
Cu	XRF	0.0019	0.0065	517	499	97%	423	82%
Zn	XRF	0.0038	0.0125	517	507	98%	472	91%
Ga	XRF	0.0032	0.0108	517	7	1%	0	0%
Ge	XRF	0.0027	0.0089	517	60	12%	9	2%
As	XRF	0.0023	0.0077	517	151	29%	47	9%
Se	XRF	0.0000	0.0000	517	1	0%	1	0%
Br	XRF	0.0020	0.0068	517	472	91%	322	62%
Rb	XRF	0.0013	0.0044	517	62	12%	1	0%
Sr	XRF	0.0023	0.0078	517	107	21%	0	0%
Y	XRF	0.0011	0.0037	517	32	6%	0	0%
Zr	XRF	0.0031	0.0102	517	111	21%	0	0%
Nb	XRF	0.0034	0.0114	517	62	12%	0	0%
Mo	XRF	0.0026	0.0086	517	278	54%	0	0%
Rh	XRF	0.0052	0.0172	517	21	4%	0	0%
Pd	XRF	0.0079	0.0262	517	6	1%	0	0%
Ag	XRF	0.0048	0.0162	517	0	0%	0	0%
Cd	XRF	0.0046	0.0154	517	32	6%	0	0%
In	XRF	0.0070	0.0235	517	3	1%	0	0%
Sn	XRF	0.0080	0.0267	517	137	26%	15	3%
Sb	XRF	0.0066	0.0219	517	94	18%	0	0%
Te	XRF	0.0112	0.0374	517	5	1%	0	0%
I	XRF	0.0139	0.0463	517	6	1%	0	0%
Cs	XRF	0.0602	0.2008	517	19	4%	0	0%
Ba	XRF	0.0776	0.2587	517	19	4%	0	0%
La	XRF	0.0806	0.2686	517	19	4%	0	0%
Ce	XRF	0.0030	0.0101	517	6	1%	0	0%
Sm	XRF	0.0027	0.0089	517	12	2%	0	0%
Eu	XRF	0.0053	0.0178	517	123	24%	0	0%
Tb	XRF	0.0031	0.0103	517	77	15%	7	1%

Species	Analytical Method	LOD (μg/m^3)	LOQ (μg/m^3)	No. of valid Values	No. > LOD	% > LOD	No. > LOQ	% > LOQ
Hf	XRF	0.0230	0.0766	517	0	0%	0	0%
Ta	XRF	0.0113	0.0378	517	102	20%	5	1%
W	XRF	0.0236	0.0786	517	18	3%	18	3%
Ir	XRF	0.0041	0.0136	517	0	0%	0	0%
Au	XRF	0.0023	0.0078	517	5	1%	0	0%
Hg	XRF	0.0027	0.0090	517	0	0%	0	0%
Tl	XRF	0.0032	0.0106	517	9	2%	0	0%
Pb	XRF	0.0045	0.0151	517	412	80%	295	57%
U	XRF	0.0053	0.0176	517	15	3%	0	0%

The number of reported concentrations for each species and number of reported concentrations greater than the LODs and LOQs are also summarized in Table 8. For the 513 valid quartz fiber filter samples and 517 valid Teflon filter samples, major ions (including nitrate, sulfate, ammonium, and soluble sodium), organic carbon, elemental carbon, sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn) were detected (> LOD) in almost all the samples (more than 90%). Several transition metals (e.g. Sc, Ga, Ge, Se, Rb, Y, Nb, Rh, Pd, Ag, Cd, In, Te, I, Cs, Ba, La, Ce, Sm, Hf, W, Ir, Au, Hg, Tl, and U) were not detected in most of the samples (less than 15%). Species from motor vehicle exhaust such as Br and Pb were detected in 91% and 80% of the samples, respectively. V and Ni, which are residual-oil-related species, were both detected in most of the samples. This is typical for urban and suburban sites in most regions. Toxic species emitted from industrial sources, such as Cd and Hg, were not detected (6% and 0% of the samples, respectively). Soil/dust-related species, including Al, Si, Ca, Ti, and Fe, were found above the LODs in more than 96% of the samples and above the LOQs in more than 78% of the samples.

In general, the analytical specifications shown in Table 8 suggest that the $PM_{2.5}$ samples collected during the study period possess adequate loadings for chemical analysis. The detection limits of the selected analytical methods were sufficiently low to establish valid measurements with acceptable precision.

3.3 Data Validation

Three levels of data validation were conducted to the data set acquired from the study.

Level I data validation: 1) flag measurements for deviations from procedures; 2) identify and remove invalid values and indicate the reasons for invalid sampling, and 3) estimate precisions from replicate and blank analyses.

Level II data validation examines internal consistency tests among different data and attempts to resolve discrepancies based on known physical relationships between variables: 1) compare a sum of chemical species to mass concentrations; 2) compare measurements from different methods; 3) compare collocated measurements; 4) examine time series from different sites to identify and investigate outliers, and 5) prepare a data qualification statement.

Level III data validation is part of the data interpretation process and should identify unusual values including: 1) extreme values; 2) values which would otherwise normally track the values of other variables in a time series, and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern. External consistency tests are used to identify values in the data set which appear atypical when compared to other data sets. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If nothing unusual is found upon tracing the path of the measurement, the value would be assumed to be a valid result of an environmental cause.

Level I data validation was performed and the validation flags and comments are stated in the database as documented in Section 3.1. Level II validation tests and results are described in the following subsections including 1) sum of chemical species versus $PM_{2.5}$ mass; 2) physical and chemical consistency; 3) anion/cation balance; 4) reconstructed versus measured mass; 5) carbon measurements by different thermal/optical methods, and 6) collocated measurement comparison. For Level III data validation, parallel consistency tests were applied to data sets from the same population (e.g., region, period of time) by different data analysis approaches. Collocated samples collected at four out of the seven sampling sites were examined. Comparison of $PM_{2.5}$ mass concentrations obtained from gravimetric analysis and from 24-hr average continuous measurements were also conducted. The level III data validation continues for as long as the database is maintained. For Level II/III data validation in this study, correlations and linear regression statistics were performed on the valid data set and scatter plots were generated for better comparison.

3.3.1 Sum of Chemical Species versus $PM_{2.5}$ Mass

The sum of the individual chemical concentrations determined in this study for $PM_{2.5}$ samples should be less than or equal to the corresponding mass concentrations obtained from gravimetric measurements. The chemical species include those that were quantified on both Teflon-membrane filters and quartz fiber filters. To avoid double counting, chloride (Cl^-), total potassium (K), soluble sodium (Na^+), and sulfate (SO_4^{2-}) are included in the sum while total sulfur (S), total chlorine (Cl), total sodium (Na), and soluble potassium (K^+) are excluded. Carbon concentration is represented by the sum of organic carbon and elemental carbon. Unmeasured ions, metal oxides, or hydrogen and oxygen associated with organic carbon are not counted into the measured concentrations.

The sum of chemical species was plotted against the measured $PM_{2.5}$ mass on Teflon filters for each of the individual sites in Figure 2. Linear regression analysis results and the average ratios of Y over X are both shown in Table 9 for comparison. Each plot contains a solid line indicating the slope with intercept and a dashed 1:1 line. Measurement uncertainties associated with the x- and y-axes are shown and the uncertainties of the $PM_{2.5}$ mass data were assumed to be 5% of the concentrations.

A strong correlation ($R^2 = 0.98$) was found between the sum of measured species and mass with a slope of 0.826±0.006.

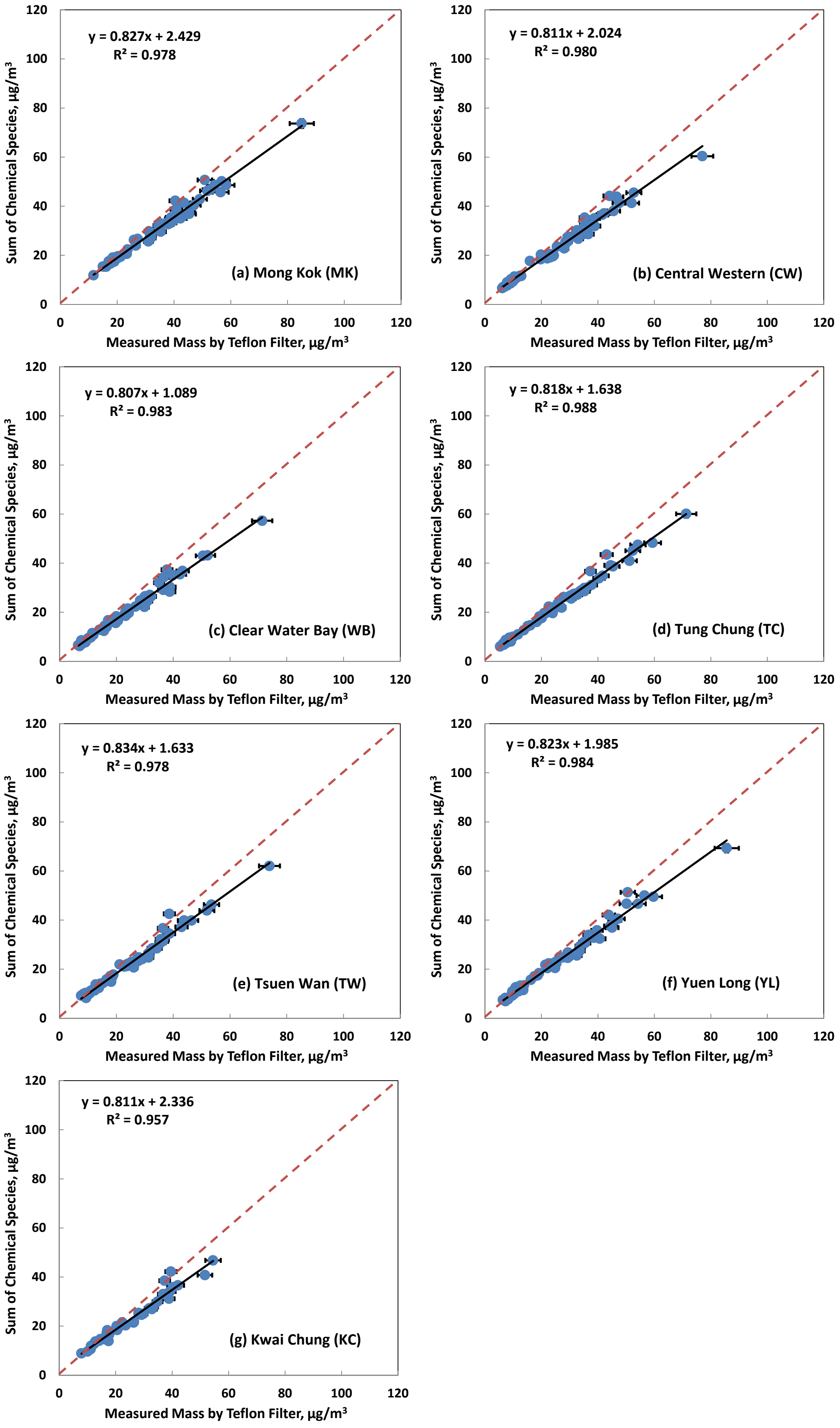


Figure 2. Scatter plots of sum of measured chemical species versus measured mass on Teflon filter for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 9. Statistics analysis of sum of measured chemical species versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Slope	0.827 (±0.015)	0.811 (±0.015)	0.807 (±0.014)	0.818 (±0.012)	0.834 (±0.017)	0.823 (±0.014)	0.811 (±0.028)	0.826 (±0.006)
Intercept	2.429 (±0.620)	2.024 (±0.455)	1.089 (±0.371)	1.638 (±0.357)	1.633 (±0.492)	1.985 (±0.445)	2.336 (±0.778)	1.677 (±0.185)
R^2	0.978	0.980	0.983	0.988	0.978	0.984	0.957	0.979
AVG mass	33.90	25.75	23.12	25.25	26.19	27.29	25.28	26.70
AVG sum	30.46	22.92	19.74	22.30	23.48	24.45	22.84	23.74
AVG sum/mass	0.914 (±0.063)	0.924 (±0.091)	0.876 (±0.076)	0.920 (±0.091)	0.919 (±0.088)	0.930 (±0.092)	0.927 (±0.090)	0.915 (±0.086)

Limits used for identifying reconstructed mass outliers are referring to those in Speciation Trends Network (STN) program suggested by USEPA [2012] and are listed as follows,

Lower Limit: [Sum of Chemical Species]/[Measured Mass] < 0.60

Upper Limit: [Sum of Chemical Species]/[Measured Mass] > 1.32

Based on these criteria, no samples were identified as outliers in this dataset.

3.3.2 Physical and Chemical Consistency

Measurements of chemical species concentrations conducted by different methods are compared. Physical and chemical consistency tests include: 1) sulfate (SO_4^{2-}) versus total sulfur (S), 2) soluble potassium (K^+) versus total potassium (K), and 3) ammonium balance.

3.3.2.1 Water-Soluble Sulfate (SO_4^{2-}) versus Total Sulfur (S)

SO_4^{2-} is measured by ion chromatography (IC) on quartz fiber filters and total S is measured by X-Ray Fluorescence (XRF) on Teflon filters. The theoretical ratio of SO_4^{2-} to S is 3, based on their molecular weights and assuming all of the sulfur is present as SO_4^{2-}. Since SO_4^{2-} and total S are collected on different filters, this ratio is helpful for diagnosing flow rate problems of the samplers.

Figure 3 shows the scatter plots of SO_4^{2-} versus total S concentrations for each of the seven sites. A good correlation ($R^2 = 0.97$) were observed for all the sites with a slope of 2.79±0.023 and an intercept of -0.024±0.082. The average sulfate to total sulfur ratio was determined to be 2.80±0.306, which meets the validation criteria (SO_4^{2-}/total S < 3.0).

Good correlations ($R^2 = 0.96–0.99$) were found for sulfate/total sulfur in $PM_{2.5}$ samples collected in individual sites. The regression statistics suggest a slope ranging from 2.63±0.066 to 2.85±0.064 and the intercepts are all at relatively low levels. The average sulfate/sulfur ratio ranges from 2.73±0.344 to 2.84±0.319 (Table 10). Both of the calculations indicate that most of the sulfur was present as soluble sulfate in $PM_{2.5}$.

Limits for outliers as suggested by USEPA [2012] are as follows,

Lower Limit: $[S]/[SO_4^{2-}] < 0.25$

Upper Limit: $[S]/[SO_4^{2-}] > 0.45$

Two samples are flagged as outliers and they were listed in Table 11 with the corresponding $[S]/[SO_4^{2-}]$ ratios.

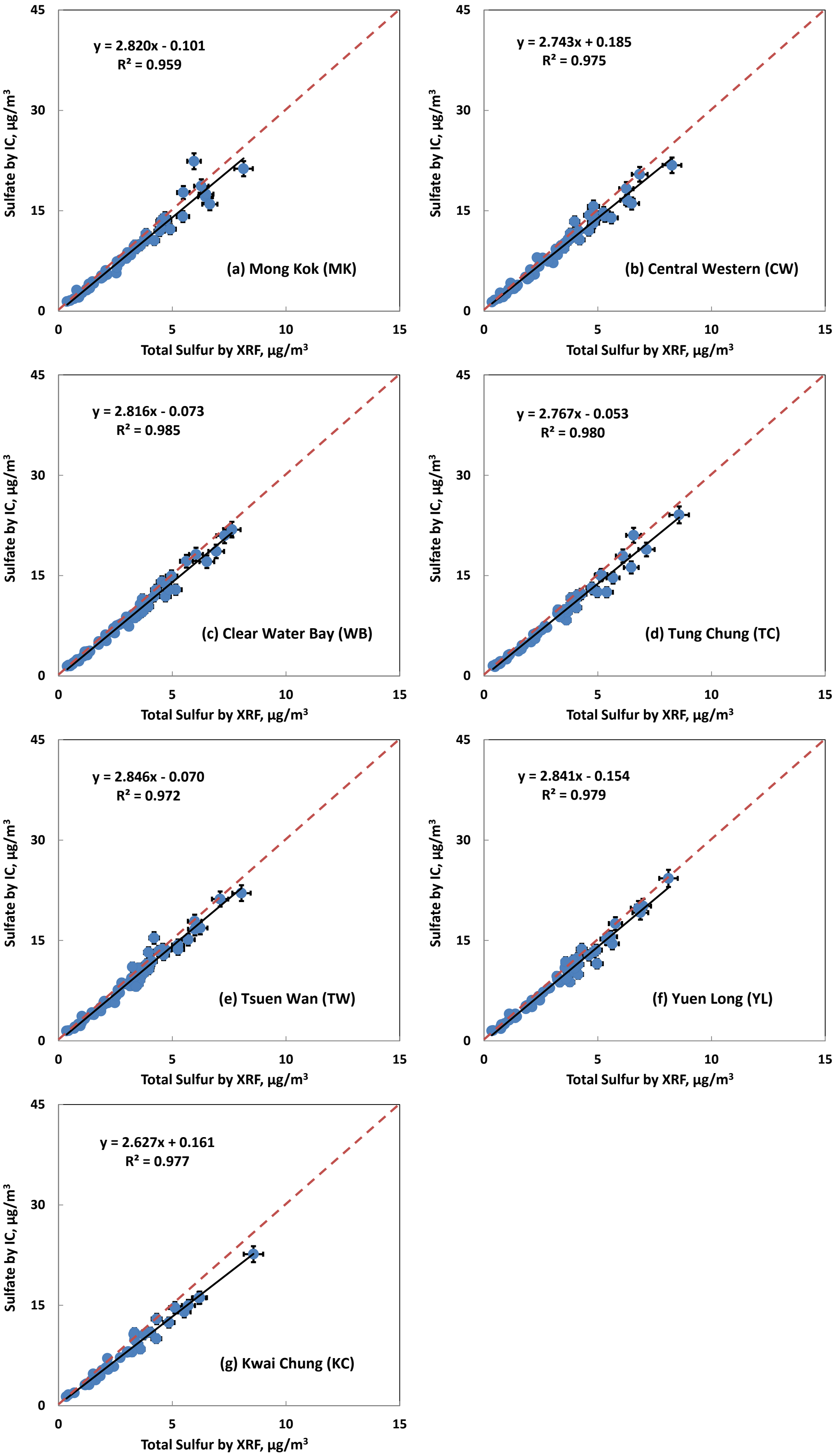


Figure 3. Scatter plots of sulfate versus total sulfur measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 10. Statistics analysis of sulfate versus total sulfur measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Slope	2.82 (±0.078)	2.74 (±0.058)	2.82 (±0.046)	2.77 (±0.053)	2.85 (±0.064)	2.84 (±0.055)	2.63 (±0.066)	2.79 (±0.023)
Intercept	-0.101 (±0.281)	0.185 (±0.209)	-0.073 (±0.162)	-0.053 (±0.192)	-0.070 (±0.224)	-0.154 (±0.197)	0.161 (±0.228)	-0.024 (±0.082)
R^2	0.959	0.975	0.985	0.980	0.972	0.979	0.977	0.974
AVG total S	3.09	3.08	3.03	3.11	3.07	3.09	2.98	3.07
AVG SO_4^{2-}	8.60	8.64	8.45	8.56	8.66	8.63	7.98	8.53
AVG SO_4^{2-}/S	2.78 (±0.317)	2.84 (±0.319)	2.81 (±0.245)	2.77 (±0.243)	2.83 (±0.328)	2.82 (±0.340)	2.73 (±0.344)	2.80 (±0.306)

Table 11. List of flagged samples from the $[S]/[SO_4^{2-}]$ test.

Sample ID	$[S]/[SO_4^{2-}]$ Ratio
TW140718	0.24
YL140718	0.23

3.3.2.2 Water-soluble Potassium (K^+) versus Total Potassium (K)

Water-soluble potassium (K^+) is measured by ion chromatography (IC) on quartz fiber filters and the total potassium (K) is measured by X-Ray Fluorescence (XRF) on Teflon filters. The ratio of K^+ to K is expected to equal or be less than 1. Figure 4 shows the scatter plots of K^+ versus total K concentrations for each of the seven sites. A good correlation ($R^2 = 0.96$) were observed for all the sites with a slope of 0.97±0.01 and an intercept of -0.022±0.004. The ratio of water-soluble potassium to total potassium averages at 0.81±0.35, which meets the validation criteria (K^+/total K < 1).

Good correlations (R^2 = 0.92–0.99) were found for K^+/K in $PM_{2.5}$ samples collected in individual sites. The regression statistics suggest a slope ranging from 0.89±0.02 to 1.00±0.03 and the intercepts are all at relatively low levels (Table 12).

Generally, almost all of the total potassium is in its soluble ionic form and a few scattered data points might be caused by instrumental and method uncertainties.

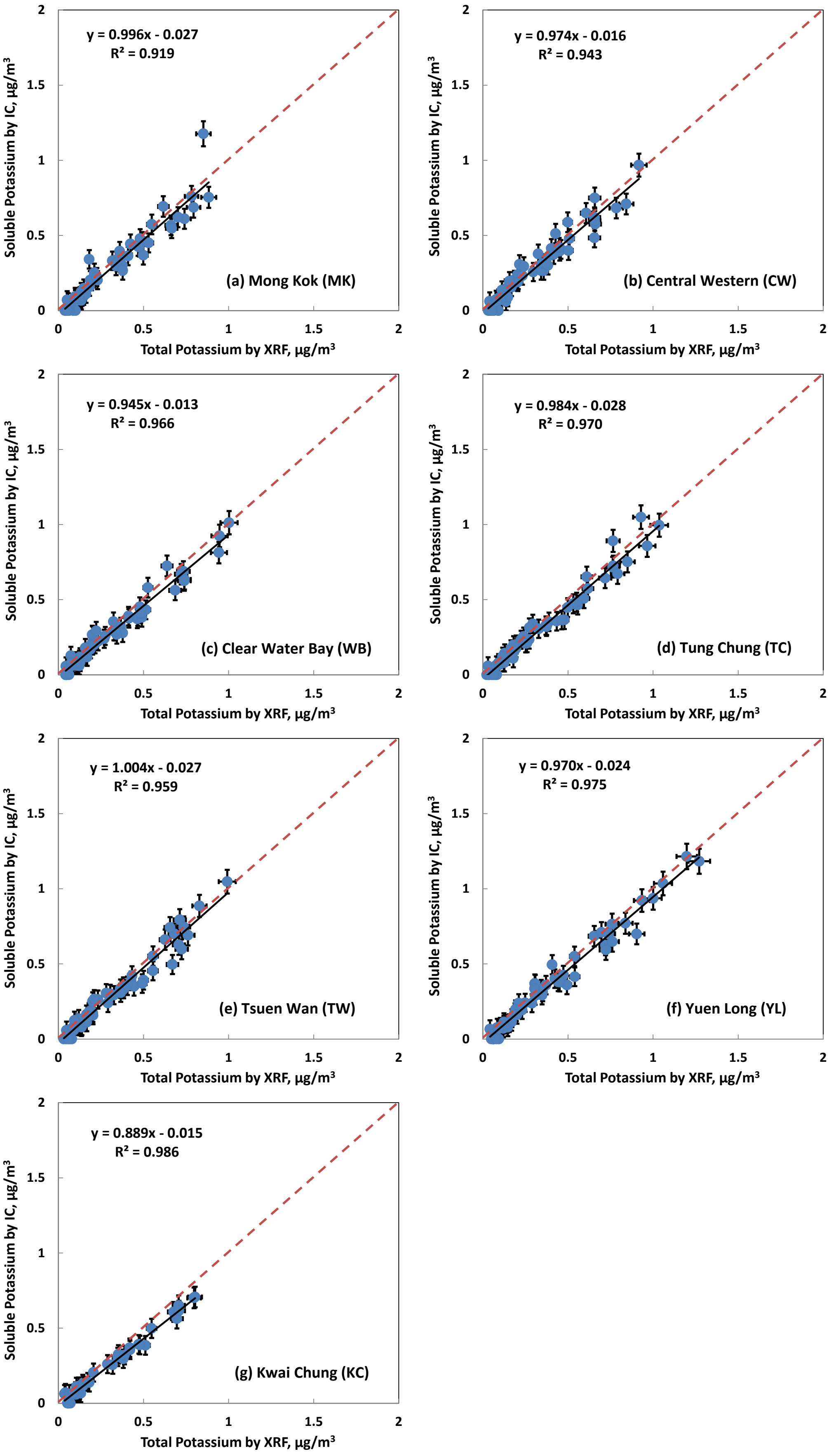


Figure 4. Scatter plots of water-soluble potassium versus total potassium measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 12. Statistics analysis of water-soluble potassium versus total potassium measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Slope	0.996 (±0.040)	0.974 (±0.032)	0.945 (±0.023)	0.984 (±0.023)	1.004 (±0.028)	0.970 (±0.021)	0.889 (±0.017)	0.970 (±0.010)
Intercept	-0.027 (±0.016)	-0.016 (±0.012)	-0.013 (±0.009)	-0.028 (±0.010)	-0.027 (±0.011)	-0.024 (±0.010)	-0.015 (±0.006)	-0.022 (±0.004)
R^2	0.919	0.943	0.966	0.970	0.959	0.975	0.986	0.959
AVG total K	0.314	0.294	0.303	0.330	0.319	0.384	0.292	0.321
AVG K^+	0.286	0.271	0.273	0.297	0.294	0.348	0.245	0.289
AVG K^+/K	0.816 (±0.353)	0.817 (±0.376)	0.822 (±0.339)	0.754 (±0.404)	0.836 (±0.303)	0.810 (±0.320)	0.802 (±0.319)	0.808 (±0.346)

3.3.2.3 Ammonium Balance

To further validate the ion measurements, calculated versus measured ammonium (NH_4^+) are compared. NH_4^+ is directly measured by IC analysis of quartz fiber filter extract. NH_4^+ is very often found in the chemical forms of NH_4NO_3, $(NH_4)_2SO_4$, and NH_4HSO_4 while NH_4Cl is usually negligible and excluded from the calculation. Assuming full neutralization, measured NH_4^+ can be compared with the computed NH_4^+, which can be calculated in the following two ways,

Calculated NH_4^+ based on NH_4NO_3 and $(NH_4)_2SO_4$ = $0.29 \times [NO_3^-] + 0.374 \times [SO_4^{2-}]$

Calculated NH_4^+ based on NH_4NO_3 and NH_4HSO_4 = $0.29 \times [NO_3^-] + 0.187 \times [SO_4^{2-}]$

The calculated NH_4^+ is plotted against measured NH_4^+ for each of the seven sites in Figure 5. For both forms of sulfate the comparisons show strong correlations ($R^2 = 0.98$ for ammonium sulfate and $R^2 = 0.97$ for ammonium bisulfate, respectively) but with quite different slopes. The slopes for individual sampling sites range from 1.00±0.02 at CW to 1.03±0.01 at WB assuming ammonium sulfate, and from 0.52±0.02 at KC to 0.60±0.01 at YL assuming ammonium bisulfate. These values were close to those found in earlier years. The average ratios of calculated ammonium to measured ammonium (see Table 13) suggest that ammonium sulfate is the dominant form for sulfate in the $PM_{2.5}$ over the Hong Kong region in the year of 2014.

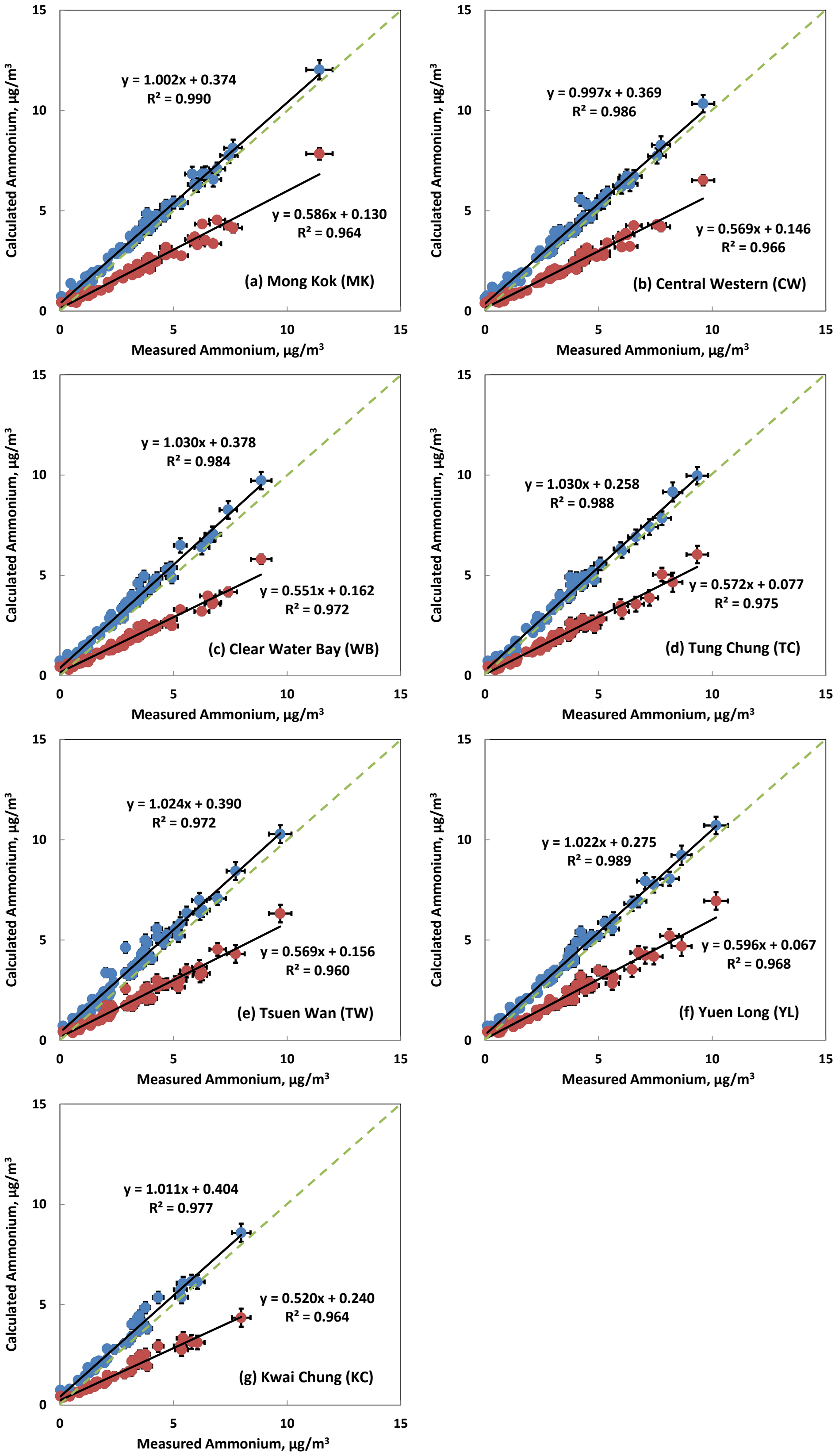


Figure 5. Scatter plots of calculated ammonium versus measured ammonium for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC. The calculated ammonium data are obtained assuming all nitrate was in the form of ammonium nitrate and all sulfate was in the form of either ammonium sulfate (data in blue) or ammonium bisulfate (data in brown).

Table 13. Statistics analysis of calculated ammonium versus measured ammonium for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Ammonium Sulfate (blue dots)								
Slope	1.00 (±0.014)	1.00 (±0.016)	1.03 (±0.017)	1.03 (±0.015)	1.02 (±0.023)	1.02 (±0.014)	1.01 (±0.025)	1.01 (±0.007)
Intercept	0.374 (±0.055)	0.369 (±0.062)	0.378 (±0.060)	0.258 (±0.056)	0.390 (±0.084)	0.275 (±0.056)	0.404 (±0.081)	0.354 (±0.024)
R^2	0.990	0.986	0.984	0.988	0.972	0.989	0.977	0.984
AVG Mea. NH_4^+	3.28	3.25	2.85	3.10	3.05	3.29	2.70	3.09
AVG Cal. NH_4^+	3.66	3.61	3.31	3.45	3.51	3.64	3.14	3.49
AVG Cal./Mea. NH_4^+	1.44 (±1.39)	1.33 (±1.02)	1.28 (±0.336)	1.24 (±0.598)	1.34 (±0.737)	1.27 (±0.763)	2.07 (±4.97)	1.39 (±1.784)
Ammonium Bisulfate (brown dots)								
Slope	0.586 (±0.015)	0.569 (±0.014)	0.551 (±0.012)	0.572 (±0.012)	0.569 (±0.015)	0.596 (±0.014)	0.520 (±0.016)	0.572 (±0.005)
Intercept	0.130 (±0.062)	0.146 (±0.055)	0.162 (±0.043)	0.077 (±0.045)	0.156 (±0.056)	0.067 (±0.058)	0.240 (±0.053)	0.127 (±0.020)
R^2	0.964	0.966	0.972	0.975	0.960	0.968	0.964	0.965
AVG Mea. NH_4^+	3.28	3.25	2.85	3.10	3.05	3.29	2.70	3.09
AVG Cal. NH_4^+	2.05	2.00	1.73	1.85	1.89	2.03	1.64	1.90
AVG Cal./Mea. NH_4^+	0.812 (±0.843)	0.739 (±0.617)	0.675 (±0.207)	0.673 (±0.380)	0.732 (±0.459)	0.708 (±0.468)	1.15 (±2.95)	0.766 (±1.065)

It is noted that the large standard deviations of the calculated-to-measured NH_4^+ ratio are caused by samples collected on July 18 and September 19, 2014 at all seven sites. On these two days, higher levels of Na^+ and Cl^- were observed while the NH_4^+ concentrations were much lower than those on other sampling days. Ammonium balance results excluding the two sets of samples are shown in Table 14.

Table 14. Statistical analysis of calculated ammonium versus measured ammonium for $PM_{2.5}$ samples collected at individual sites (excluding samples collected on 20140718 and 20140916).

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	55	58	58	57	57	57	38	380
Ammonium Sulfate (blue dots)								
Slope	1.01 (±0.014)	1.00 (±0.016)	1.04 (±0.018)	1.03 (±0.015)	1.03 (±0.024)	1.03 (±0.015)	1.02 (±0.027)	1.02 (±0.007)
Intercept	0.347 (±0.058)	0.334 (±0.065)	0.357 (±0.063)	0.245 (±0.059)	0.368 (±0.090)	0.247 (±0.059)	0.368 (±0.088)	0.329 (±0.026)
R^2	0.990	0.985	0.984	0.988	0.970	0.989	0.976	0.984
AVG Mea. NH_4^+	3.40	3.36	2.94	3.20	3.15	3.40	2.84	3.20
AVG Cal. NH_4^+	3.77	3.71	3.40	3.55	3.61	3.74	3.27	3.59
AVG Cal./Mea. NH_4^+	1.20 (±0.279)	1.21 (±0.376)	1.26 (±0.305)	1.17 (±0.183)	1.21 (±0.194)	1.15 (±0.146)	1.21 (±0.169)	1.20 (±0.253)
Ammonium Bisulfate (brown dots)								
Slope	0.591 (±0.016)	0.576 (±0.015)	0.556 (±0.013)	0.576 (±0.012)	0.574 (±0.016)	0.602 (±0.015)	0.525 (±0.018)	0.578 (±0.006)
Intercept	0.102 (±0.065)	0.116 (±0.058)	0.142 (±0.045)	0.058 (±0.047)	0.133 (±0.060)	0.038 (±0.060)	0.218 (±0.058)	0.102 (±0.022)
R^2	0.963	0.965	0.972	0.975	0.958	0.967	0.961	0.965
AVG Mea. NH_4^+	3.40	3.36	2.94	3.20	3.15	3.40	2.84	3.20
AVG Cal. NH_4^+	2.11	2.05	1.78	1.90	1.94	2.08	1.71	1.95
AVG Cal./Mea. NH_4^+	0.668 (±0.165)	0.664 (±0.221)	0.661 (±0.182)	0.624 (±0.114)	0.650 (±0.116)	0.634 (±0.092)	0.637 (±0.099)	0.649 (±0.150)

3.3.3 Charge Balance

For the anion and cation balance, the sum of Cl^-, NO_3^-, and SO_4^{2-} is compared to the sum of NH_4^+, Na^+, and K^+ in μeq/m^3 using the following equations:

$$\mu eq/m^3 \text{ for anions } = \left(\frac{Cl^-}{35.453} + \frac{NO_3^-}{62.005} + \frac{SO_4^{2-}}{96/2} \right)$$

$$\mu eq/m^3 \text{ for cations } = \left(\frac{NH_4^+}{18.04} + \frac{Na^+}{23.0} + \frac{K^+}{39.098} \right)$$

The cation equivalents are plotted against the anion equivalents in Figure 6. A strong correlation ($R^2 = 0.99$) was observed for the $PM_{2.5}$ samples collected at all of the sampling sites. Seen from Figure 6, the slopes obtained from individual sites range from 0.96±0.01 to 0.98±0.01 while the average Σanion/Σcation ratios range from 1.01±0.10 to 1.06±0.15 (Table 15).

The limits used for identifying outliers suggested by USEPA [2012] are as follows,

Lower Limit: [Sum of Anions]/[Sum of Cations] < 0.86

Upper Limit: [Sum of Anions]/[Sum of Cations] > 2.82

Based on these criteria, no samples were identified as outliers in this dataset.

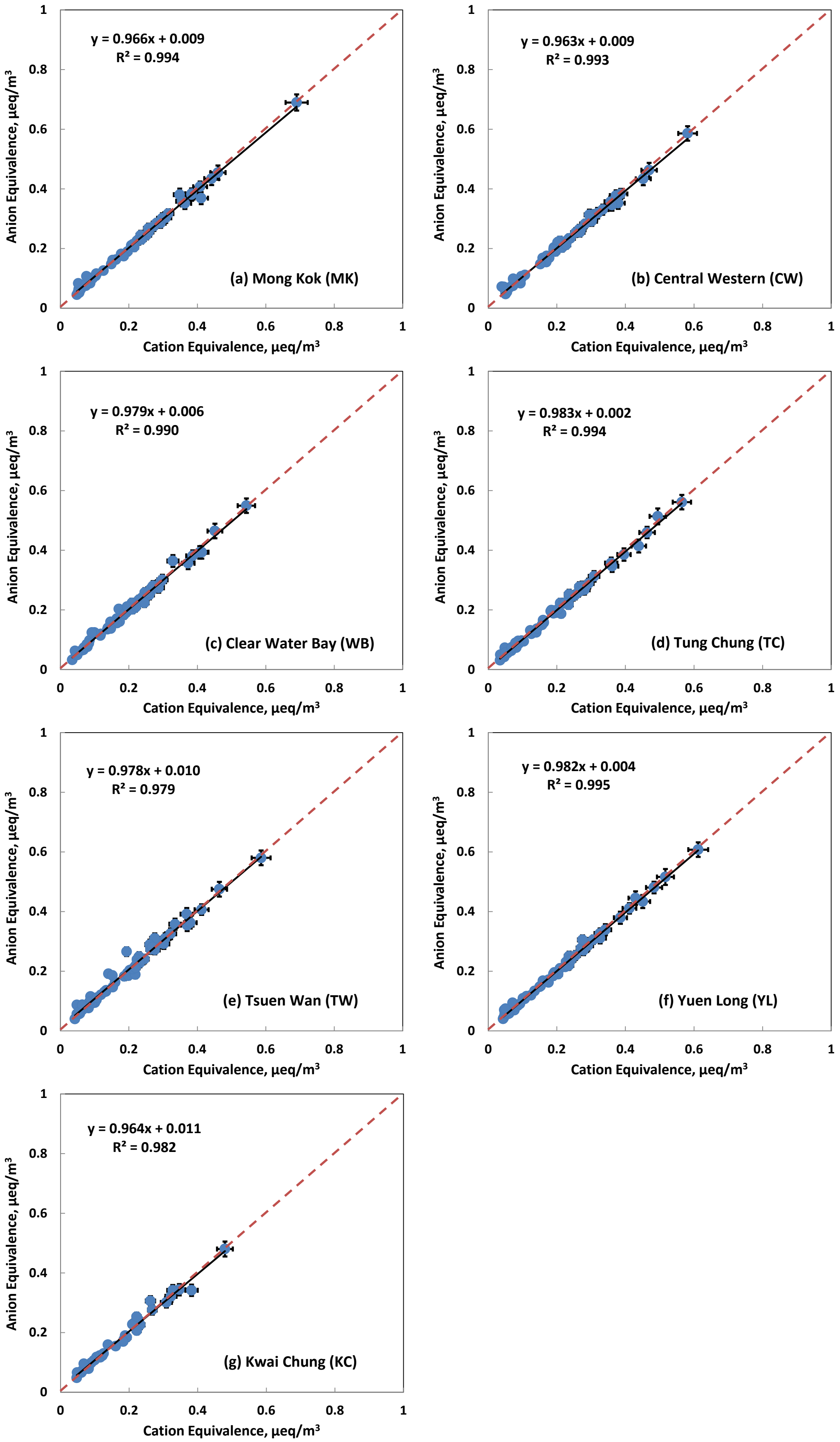


Figure 6. Scatter plots of anion versus cation measurements for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 15. Statistics analysis of anion versus cation measurements for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Slope	0.966 (±0.010)	0.963 (±0.011)	0.979 (±0.013)	0.983 (±0.010)	0.978 (±0.019)	0.982 (±0.009)	0.964 (±0.021)	0.974 (±0.005)
Intercept	0.009 (±0.003)	0.009 (±0.003)	0.006 (±0.003)	0.002 (±0.002)	0.010 (±0.004)	0.004 (±0.002)	0.011 (±0.004)	0.007 (±0.001)
R^2	0.994	0.993	0.990	0.994	0.979	0.995	0.982	0.990
AVG Σcation	0.207	0.205	0.186	0.197	0.194	0.207	0.174	0.197
AVG Σanion	0.210	0.206	0.188	0.196	0.199	0.207	0.179	0.199
AVG Σanion/Σcation	1.043 (±0.118)	1.040 (±0.148)	1.031 (±0.097)	1.010 (±0.104)	1.058 (±0.150)	1.022 (±0.113)	1.053 (±0.102)	1.036 (±0.121)

3.3.4 NIOSH_TOT versus IMPROVE_A_TOR for Carbon Measurements

Carbon concentrations were determined for the collected $PM_{2.5}$ samples by both NIOSH_TOT and IMPROVE_A_TOR methods. The total carbon concentrations obtained from NIOSH_TOT and IMPROVE_A_TOR reach an excellent agreement (Figure 7), giving credence to the validities of the analysis results from both methods. The comparison results of OC and EC determined by both methods for individual sites are shown in Figure 8. Generally, EC concentrations derived by NIOSH_TOT method were much lower than those by IMPROVE_A_TOR method. The difference in EC obtained by these two protocols has been well-documented and is primarily a result of protocol-dependent nature of correction of charring of OC formed during thermal analysis [e.g., Chow et al.,2004; Chen et al., 2004; Subraminan et al., 2006]. Seen from the results, the average ratios of NIOSH_TOT EC to IMPROVE_A_TOR EC for samples from individual sampling sites range from 0.32±0.13 at WB to 0.58±0.18 at MK (Table 16). No correlation was found between NIOSH_TOT EC and IMPROVE_A_TOR EC for samples collected at Mong Kok site, which have very high EC loading on the quartz fiber filters.

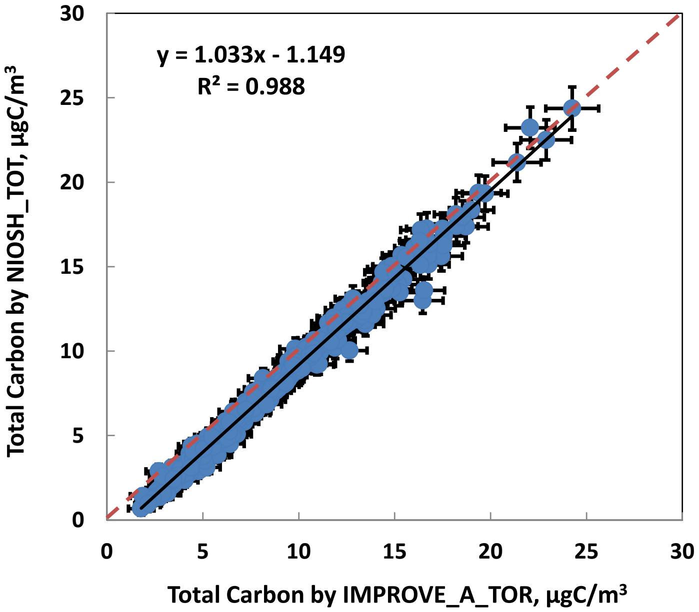
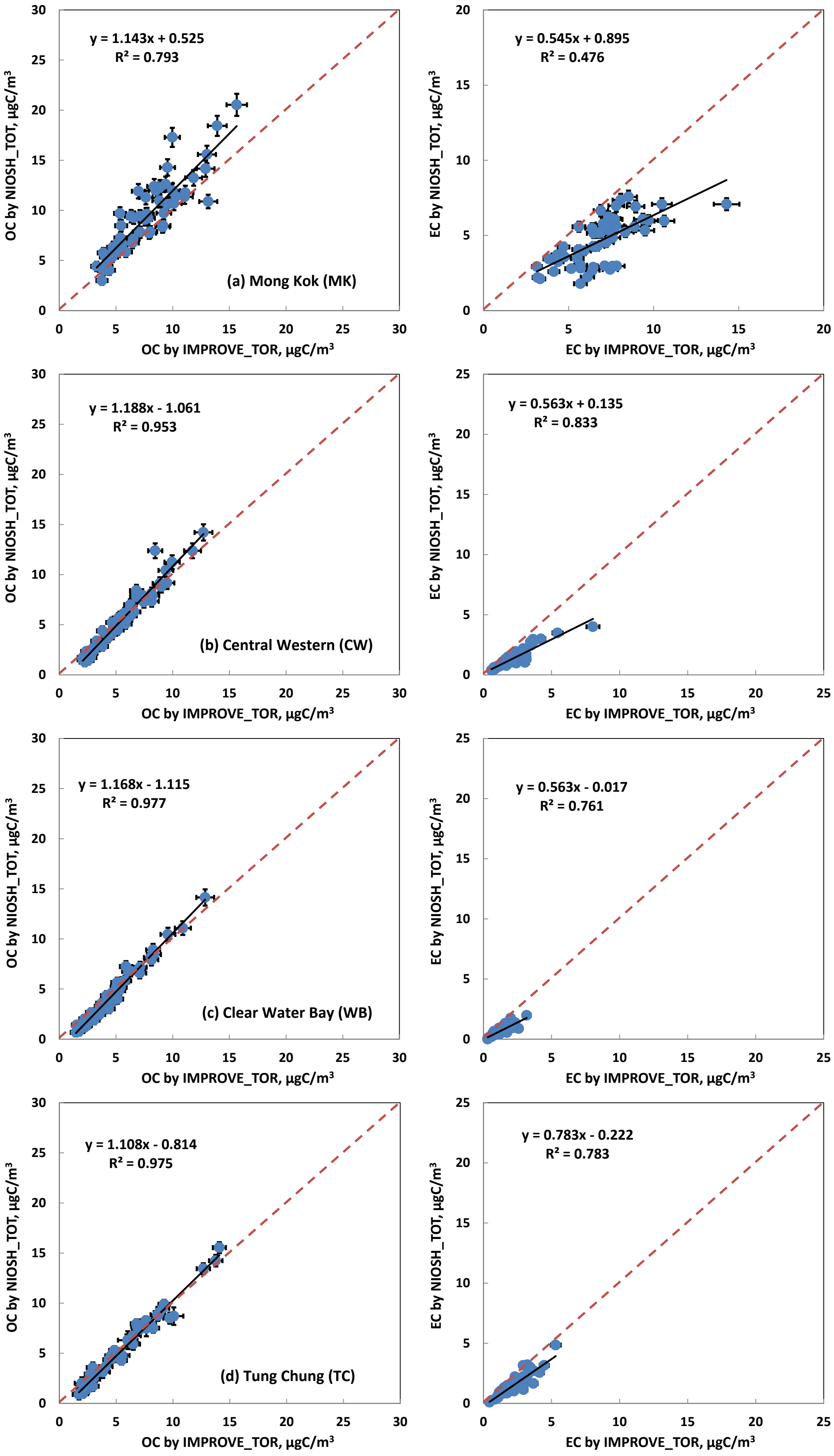


Figure 7. Comparisons of total carbon determined by NIOSH_TOT and IMPROVE_A_TOR methods for $PM_{2.5}$ samples collected at all sites.


y = 1.143x + 0.525
R² = 0.793
(a) Mong Kok (MK)
OC by NIOSH_TOT, µgC/m³
OC by IMPROVE_TOR, µgC/m³
y = 0.545x + 0.895
R² = 0.476
EC by NIOSH_TOT, µgC/m³
EC by IMPROVE_TOR, µgC/m³
y = 1.188x - 1.061
R² = 0.953
(b) Central Western (CW)
OC by NIOSH_TOT, µgC/m³
OC by IMPROVE_TOR, µgC/m³
y = 0.563x + 0.135
R² = 0.833
EC by NIOSH_TOT, µgC/m³
EC by IMPROVE_TOR, µgC/m³
y = 1.168x - 1.115
R² = 0.977
(c) Clear Water Bay (WB)
OC by NIOSH_TOT, µgC/m³
OC by IMPROVE_TOR, µgC/m³
y = 0.563x - 0.017
R² = 0.761
EC by NIOSH_TOT, µgC/m³
EC by IMPROVE_TOR, µgC/m³
y = 1.108x - 0.814
R² = 0.975
(d) Tung Chung (TC)
OC by NIOSH_TOT, µgC/m³
OC by IMPROVE_TOR, µgC/m³
y = 0.783x - 0.222
R² = 0.783
EC by NIOSH_TOT, µgC/m³
EC by IMPROVE_TOR, µgC/m³
0
5
10
15
20
25
30

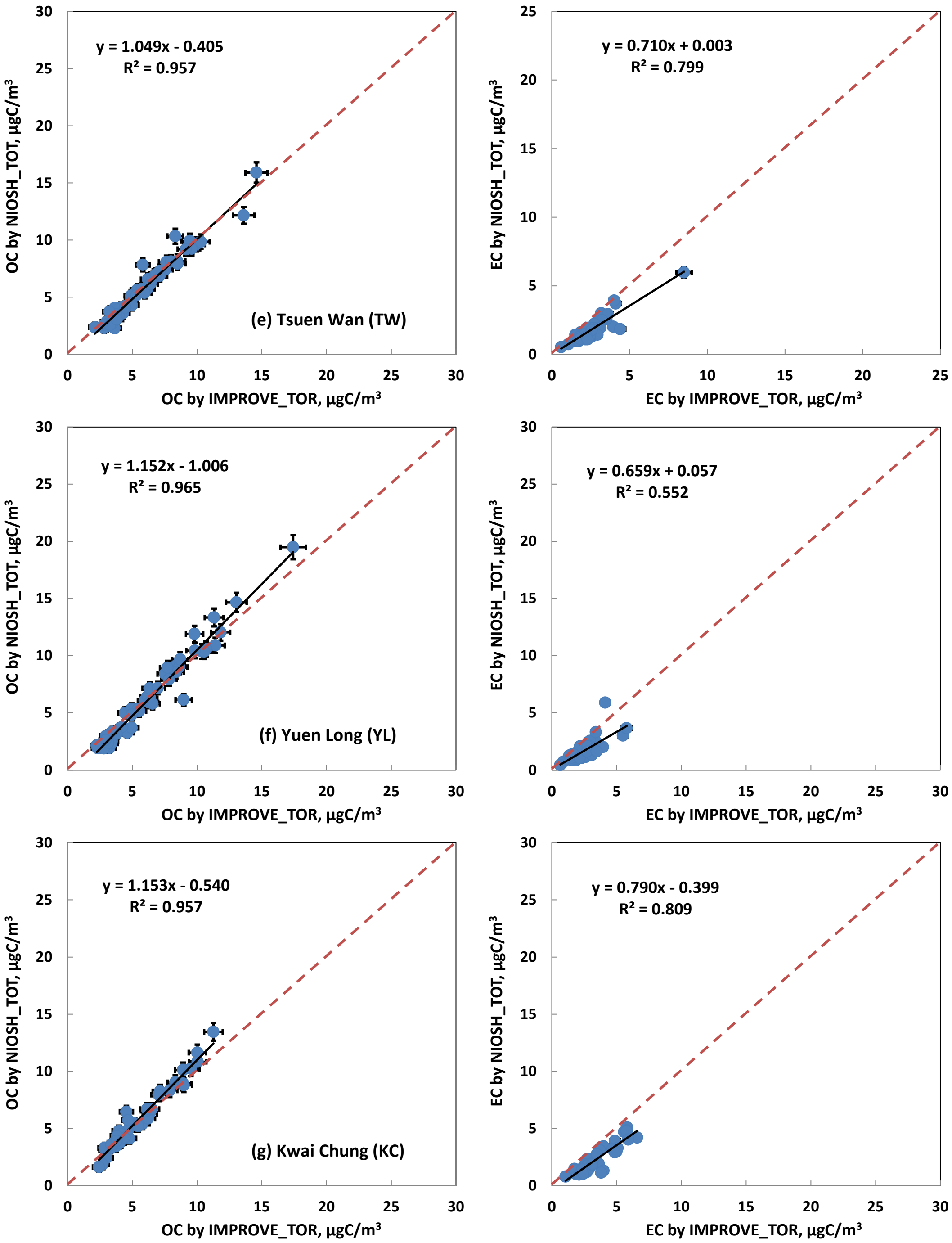


Figure 8. Comparisons of OC and EC determined by NIOSH_TOT and IMPROVE_A_TOR methods for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 16. Statistics analysis of OC and EC determined by NIOSH_TOT and IMPROVE_A_TOR methods for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
NIOSH_TOT OC versus IMPROVE_A_TOR OC								
Slope	1.14 (±0.079)	1.19 (±0.035)	1.17 (±0.023)	1.11 (±0.023)	1.05 (±0.029)	1.15 (±0.029)	1.15 (±0.040)	1.18 (±0.017)
Intercept	0.53 (±0.643)	-1.061 (±0.202)	-1.115 (±0.117)	-0.814 (±0.142)	-0.405 (±0.187)	-1.01 (±0.202)	-0.540 (±0.242)	-0.922 (±0.110)
R^2	0.793	0.953	0.977	0.975	0.957	0.965	0.957	0.924
AVG TOR_OC	7.64	5.27	4.39	5.26	5.83	6.15	5.61	5.73
AVG TOT_OC	9.26	5.20	4.01	5.02	5.71	6.07	5.93	5.86
AVG TOT_OC/TOR_OC	1.22 (±0.218)	0.932 (±0.172)	0.838 (±0.188)	0.891 (±0.183)	0.964 (±0.113)	0.945 (±0.145)	1.04 (±0.138)	0.970 (±0.204)
NIOSH_TOT EC versus IMPROVE_A_TOR EC								
Slope	0.545 (±0.077)	0.563 (±0.033)	0.563 (±0.041)	0.783 (±0.055)	0.710 (±0.047)	0.659 (±0.079)	0.790 (±0.062)	0.671 (±0.014)
Intercept	0.895 (±0.553)	0.135 (±0.082)	-0.017 (±0.059)	-0.222 (±0.132)	0.003 (±0.133)	0.057 (±0.214)	-0.399 (±0.235)	-0.010 (±0.051)
R^2	0.476	0.833	0.761	0.783	0.799	0.552	0.809	0.853
AVG TOR_EC	6.91	2.15	1.29	2.22	2.61	2.57	3.50	2.99
AVG TOT_EC	4.66	1.34	0.71	1.52	1.86	1.75	2.37	1.99
AVG TOT_EC/TOR_EC	0.683 (±0.168)	0.637 (±0.119)	0.532 (±0.165)	0.662 (±0.171)	0.712 (±0.130)	0.686 (±0.167)	0.664 (±0.149)	0.653 (±0.163)

3.3.5 Material Balance

Major PM components can be classified into seven categories including: 1) geological material, which can be estimated by (1.89 × [Al] + 2.14 × [Si] + 1.4 × [Ca] + 1.43 × [Fe]); 2) organic matter, which can be estimated from OC concentration as [OM] = 1.4 × [OC]; 3) soot which can be represented by EC concentration; 4) ammonium; 5) sulfate; 6) nitrate; 7) non-crustal trace elements; and 8) Unidentified material. Considering the large uncertainty in Na measurement by XRF, soluble sodium is used in calculation instead of total sodium. Therefore, the reconstructed mass is calculated by the following equation,

$$
\begin{aligned}
&[\text{Reconstructed Mass}] \\
= \quad & 1.89 \times [\text{Al}] + 2.14 \times [\text{Si}] + 1.4 \times [\text{Ca}] + 1.43 \times [\text{Fe}] \\
+ \quad & 1.4 \times [\text{OC}] \\
+ \quad & [\text{EC}] \\
+ \quad & [\text{NH}_4^+] \\
+ \quad & [\text{Na}^+] \\
+ \quad & [\text{K}] \\
+ \quad & [\text{SO}_4^{2-}] \\
+ \quad & [\text{NO}_3^-] \\
+ \quad & \text{trace elements excluding Na, Al, Si, K, Ca, Fe, and S}
\end{aligned}
$$

The reconstructed mass is plotting against the measured mass in Figure 9. A strong correlation ($R^2 = 0.98$) is observed between the reconstructed mass and measured mass with a slope of 0.92±0.01. Different from the comparison made between sum of chemical species and measured mass (Figure 2), the major uncertainty of the reconstructed mass is due to the estimation of organic matter (OM). Generally, the concentration of OM is determined by multiplying the OC concentration by an empirical factor. It is worth noting that the [OM]/[OC] ratio is site dependent. The [OM]/[OC] ratio of freshly emitted aerosols is usually smaller than that of the more aging (oxygenated) aerosols. In this study where a value of 1.4 was applied to this factor, it can be seen from Table 17 that the reconstructed masses at all the sites agree very well with the measured masses.

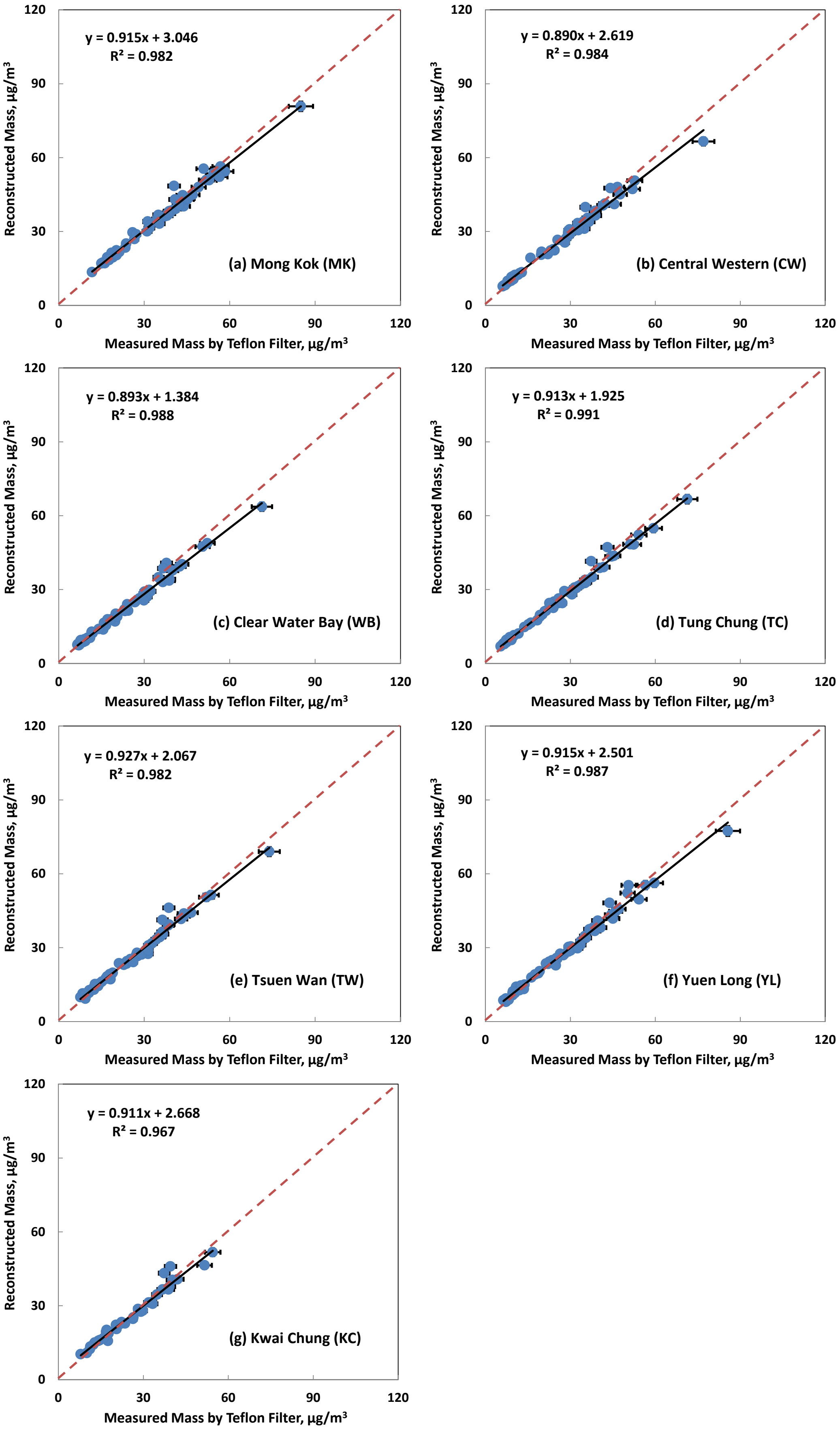


Figure 9. Scatter plots of reconstructed mass versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

Table 17. Statistics analysis of reconstructed mass versus measured mass on Teflon filters for $PM_{2.5}$ samples collected at individual sites.

Statistics/Site	MK	CW	WB	TC	TW	YL	KC	ALL
n	57	60	60	59	59	59	40	394
Slope	0.915 (±0.017)	0.890 (±0.015)	0.893 (±0.013)	0.913 (±0.012)	0.927 (±0.016)	0.915 (±0.014)	0.911 (±0.027)	0.917 (±0.006)
Intercept	3.046 (±0.623)	2.619 (±0.446)	1.384 (±0.350)	1.925 (±0.341)	2.067 (±0.482)	2.501 (±0.440)	2.668 (±0.758)	2.097 (±0.185)
R^2	0.982	0.984	0.988	0.991	0.982	0.987	0.967	0.983
AVG Mea. Mass	33.90	25.75	23.12	25.25	26.19	27.29	25.28	26.70
AVG Rec. Mass	34.06	25.54	22.04	24.98	26.35	27.47	25.69	26.58
AVG Rec./Mea. Mass	1.023 (±0.068)	1.037 (±0.108)	0.984 (±0.089)	1.034 (±0.106)	1.033 (±0.094)	1.049 (±0.105)	1.043 (±0.095)	1.028 (±0.098)

The annual average composition (%) of the major components to the $PM_{2.5}$ mass is shown in Figure 10 for individual sites. Overall, the reconstructed mass agrees very well with the measured mass using an [OM]-to-[OC] ratio of 1.4.

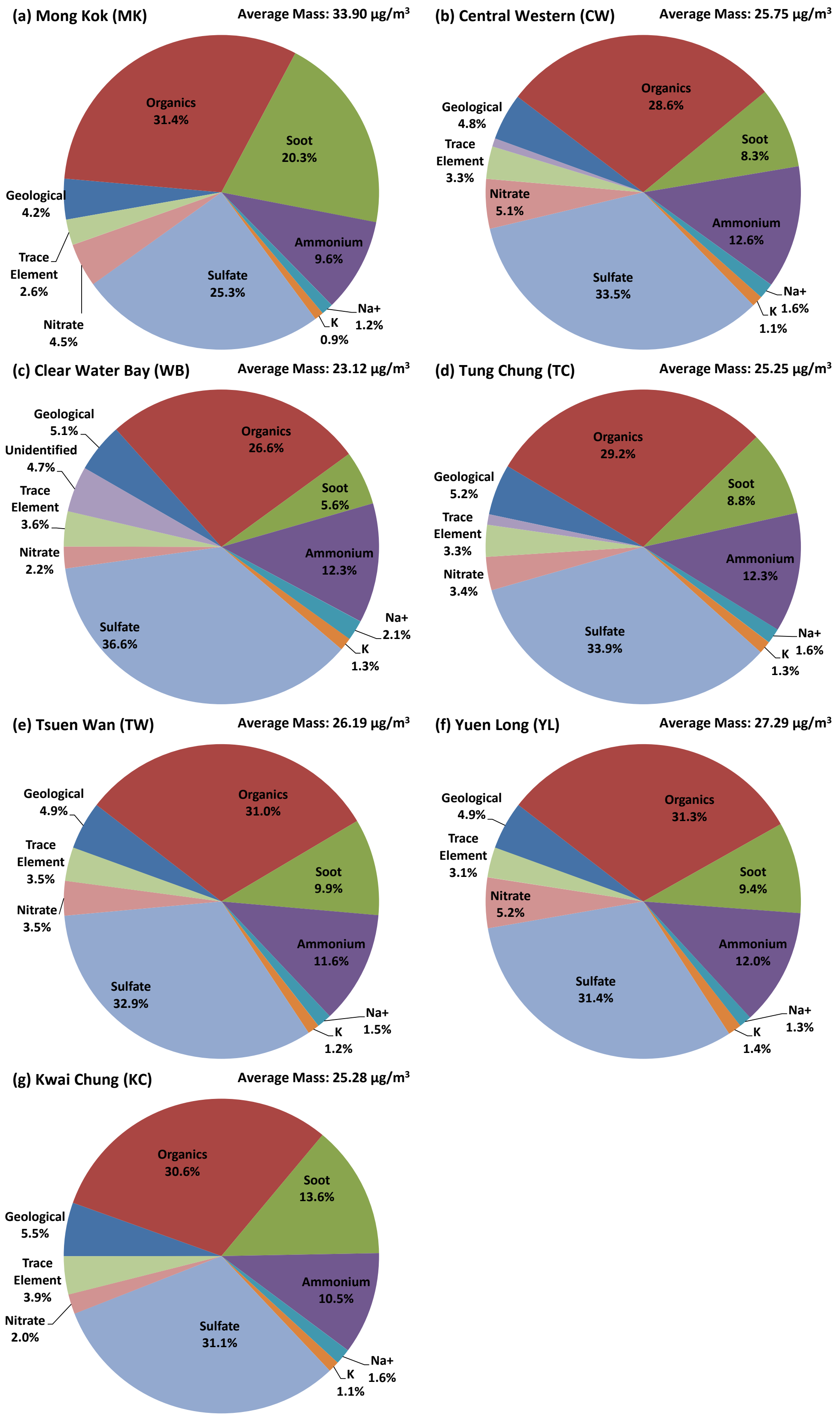


Figure 10. Annual average composition (%) of major components including 1) geological material; 2) organic matter; 3) soot; 4) ammonium; 5) sulfate; 6) nitrate; 7) non-crustal trace elements, and 8) Unidentified material (difference between measured mass and the reconstructed mass) to $PM_{2.5}$ mass for (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC).

Annually MK had the highest $PM_{2.5}$ loading while WB had the lowest (Figure 11). For all of the six sites, sulfate and OM were the two most abundant components followed by ammonium and soot (EC by IMPROVE_A_TOR method). The EC concentration was the highest at MK and the lowest at WB, which is consistent with their respective site characteristics. The concentrations of sulfate, ammonium, geological materials, and trace elements did not vary much across all six sites.

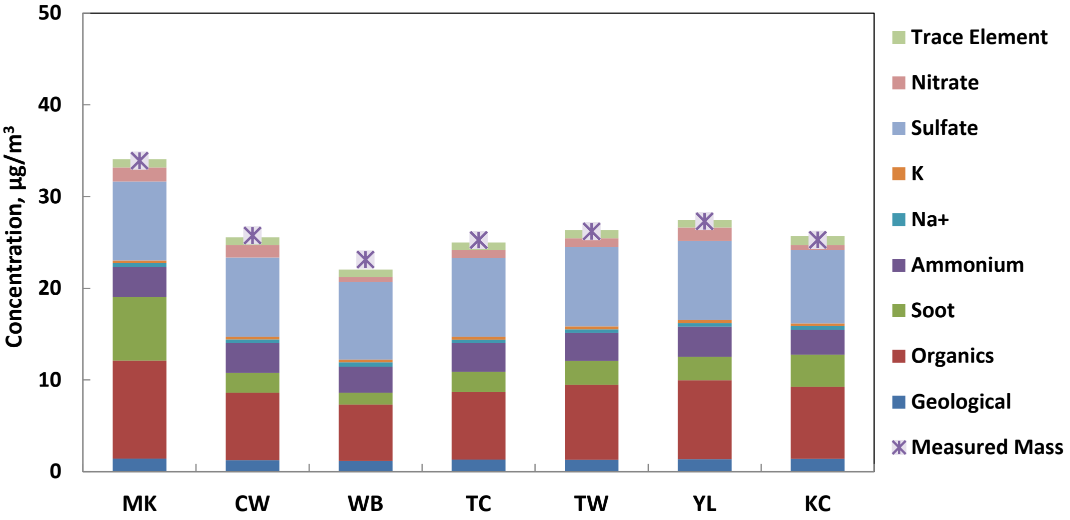


Figure 11. Comparison of annual average concentrations of major components including 1) geological material; 2) organic matter; 3) soot; 4) ammonium; 5) water-soluble sodium; 6) potassium; 7) sulfate; 8) nitrate, and 9) non-crustal trace elements and the $PM_{2.5}$ mass between individual sites.

3.3.6 Analysis of Collocated Data

In the Hong Kong $PM_{2.5}$ speciation network, four sites were equipped with collocated samplers during 2014, as shown in Table 2. The MK and CW sites included a third Partisol sampler for Teflon filters while the WB and TC sites included a third Partisol sampler for quartz fiber filters. The collocated samplers run on a 1-in-6 day schedule as the primary samplers did. The data from the sites with collocated samplers offers an opportunity to calculate total precision and compare the values with the uncertainty values that are currently being reported to HKEPD.

The data used for comparison were subject to a data screening procedure including two steps. First, species that can be quantified (concentration > 2×LOD) more than 70% of the time will be included. Second, if either of the values in one pair of samples is below the LOQ, the whole pair of samples will be removed from the data set.

Figures 12–21 show examples of the comparisons for $PM_{2.5}$ mass by gravimetric analysis, sulfur, potassium, and calcium by XRF, ammonium and sulfate by IC, OC and EC by NIOSH_TOT and IMPROVE_A_TOR, respectively. The least-squares linear regression parameters (slope, intercept, and R^2) by sites for each of these species are also included in the tables placed right below the respective figures (Tables 18–27). These figures demonstrate from good to excellent agreement for the major analytes.

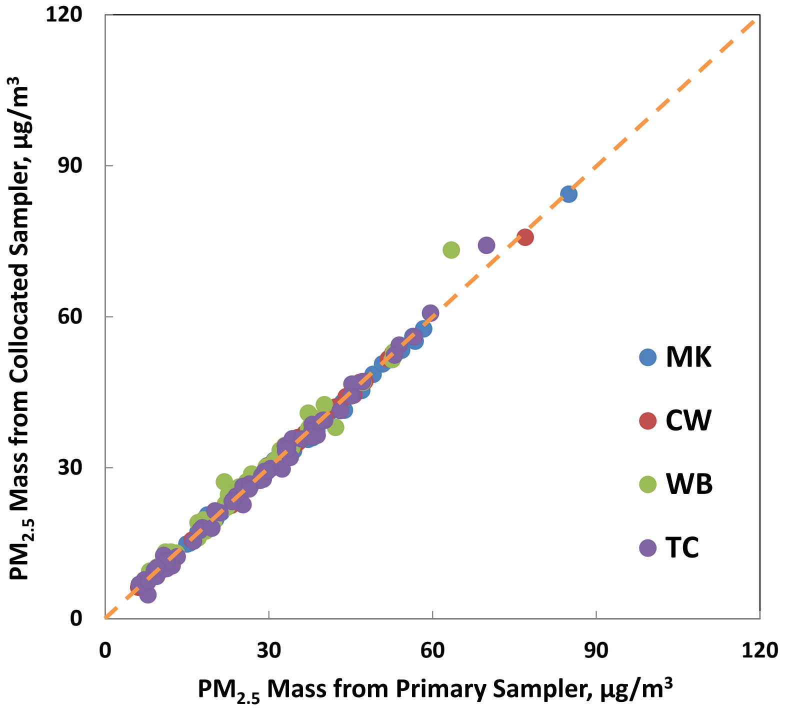


Figure 12. Collocated data for PM$_{2.5}$ mass concentration at MK, CW, WB and TC sites during 2014.

Table 18. Statistics analysis of collocated data for PM$_{2.5}$ mass concentration at MK, CW, WB and TC sites during 2014.

Statistics/Site	MK	CW	WB	TC
n	114	120	118	120
Slope	0.980 (±0.006)	0.991 (±0.003)	1.02 (±0.018)	1.01 (±0.102)
Intercept	0.302 (±0.219)	0.169 (±0.104)	0.079 (±0.487)	-0.623 (±0.318)
R^2	0.998	0.999	0.984	0.994

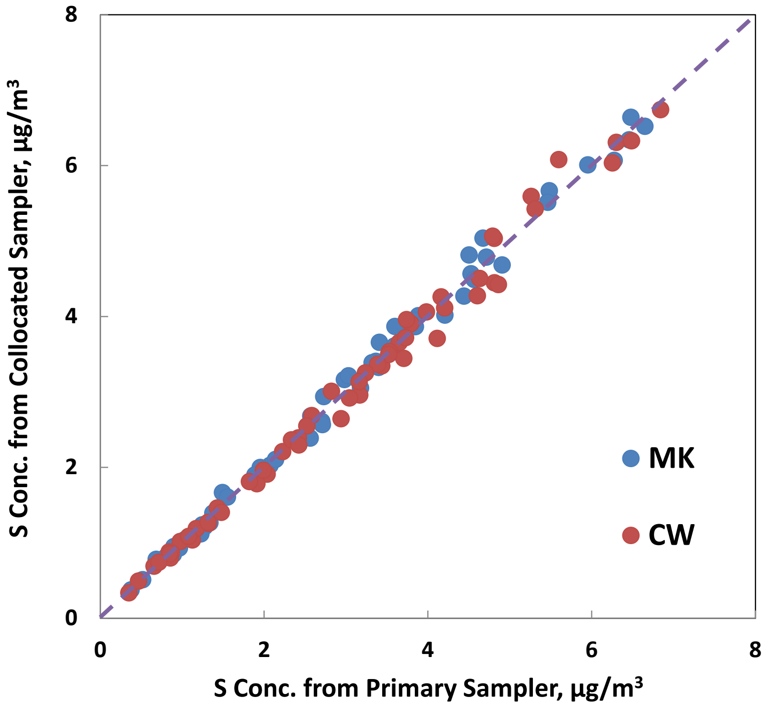


Figure 13. Collocated data for sulfur concentration at MK and CW sites during 2014.

Table 19. Statistics analysis of collocated data for sulfur concentration at MK and CW sites during 2014.

Statistics/Site	MK	CW
n	114	120
Slope	1.00 (±0.010)	0.993 (±0.012)
Intercept	0.013 (±0.034)	-0.011 (±0.042)
R^2	0.995	0.992

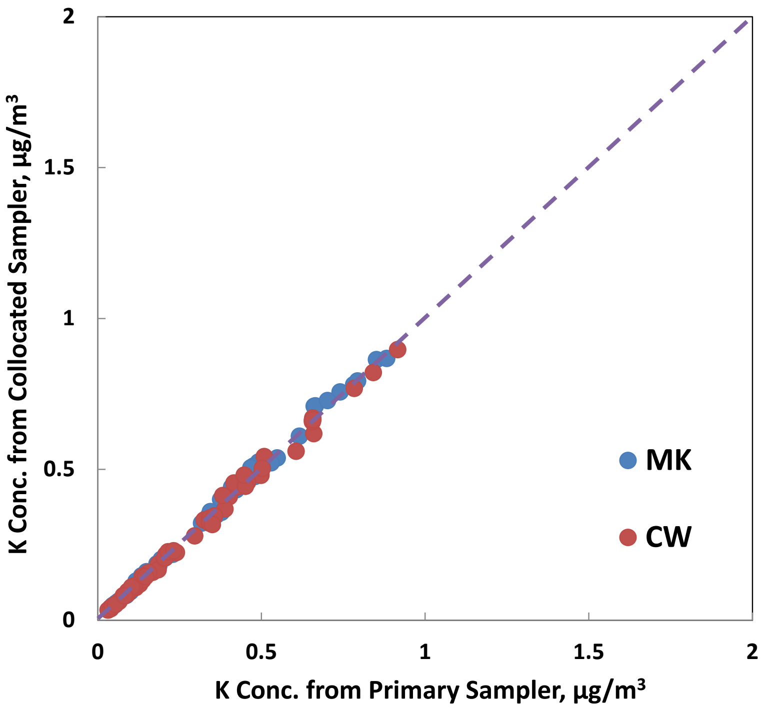


Figure 14. Collocated data for potassium concentration at MK and CW sites during 2014.

Table 20. Statistics analysis of collocated data for potassium concentration at MK and CW sites during 2014.

Statistics/Site	MK	CW
n	114	120
Slope	1.02 (±0.008)	0.987 (±0.009)
Intercept	0.000 (±0.003)	0.001 (±0.003)
R^2	0.997	0.995

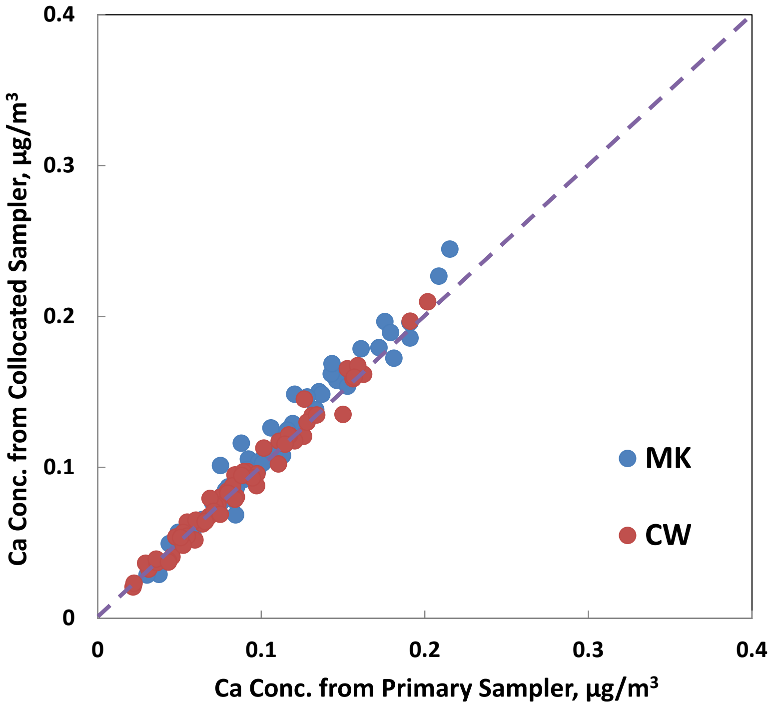


Figure 15. Collocated data for calcium concentration at MK and CW sites during 2014.

Table 21. Statistics analysis of collocated data for calcium concentration at MK and CW sites during 2014.

Statistics/Site	MK	CW
n	114	120
Slope	1.08 (±0.027)	1.02 (±0.018)
Intercept	-0.001 (±0.003)	0.000 (±0.002)
R^2	0.968	0.982

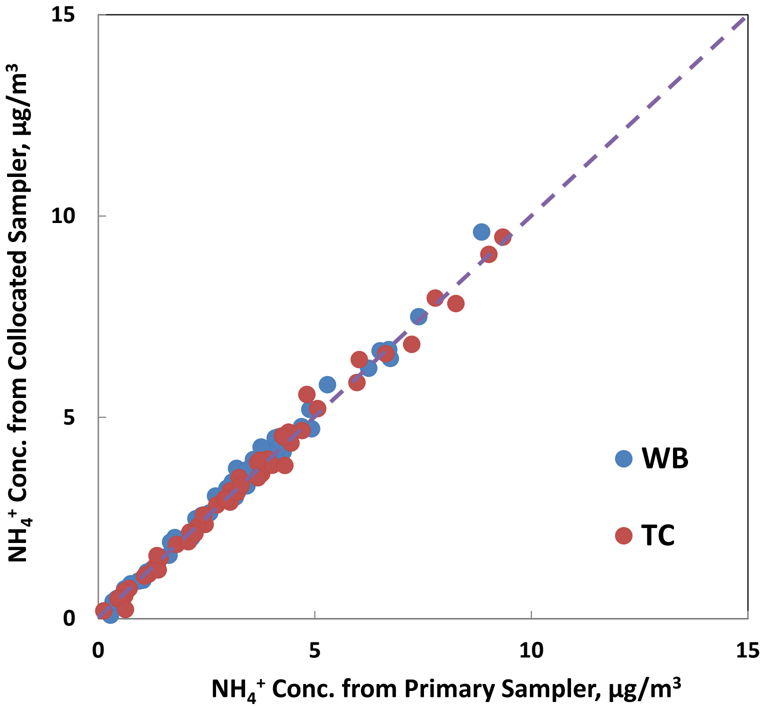


Figure 16. Collocated data for ammonium concentration at WB and TC sites during 2014.

Table 22. Statistics analysis of collocated data for ammonium concentration at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	118	122
Slope	1.03 (±0.013)	1.00 (±0.012)
Intercept	0.021 (±0.047)	-0.008 (±0.044)
R^2	0.991	0.992

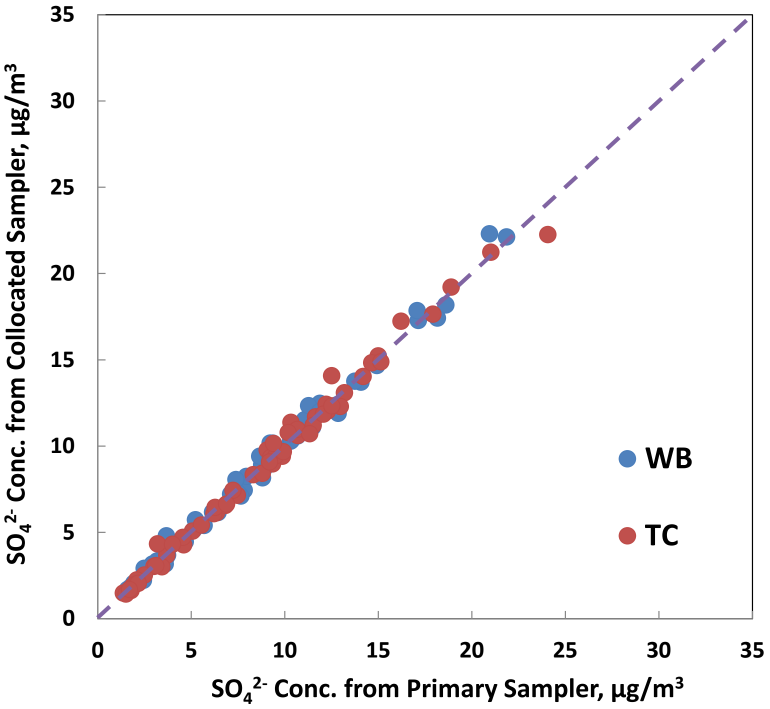


Figure 17. Collocated data for sulfate concentration at WB and TC sites during 2014.

Table 23. Statistics analysis of collocated data for sulfate concentration at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	120	122
Slope	1.00 (±0.012)	0.990 (±0.012)
Intercept	0.041 (±0.119)	0.086 (±0.117)
R^2	0.992	0.992

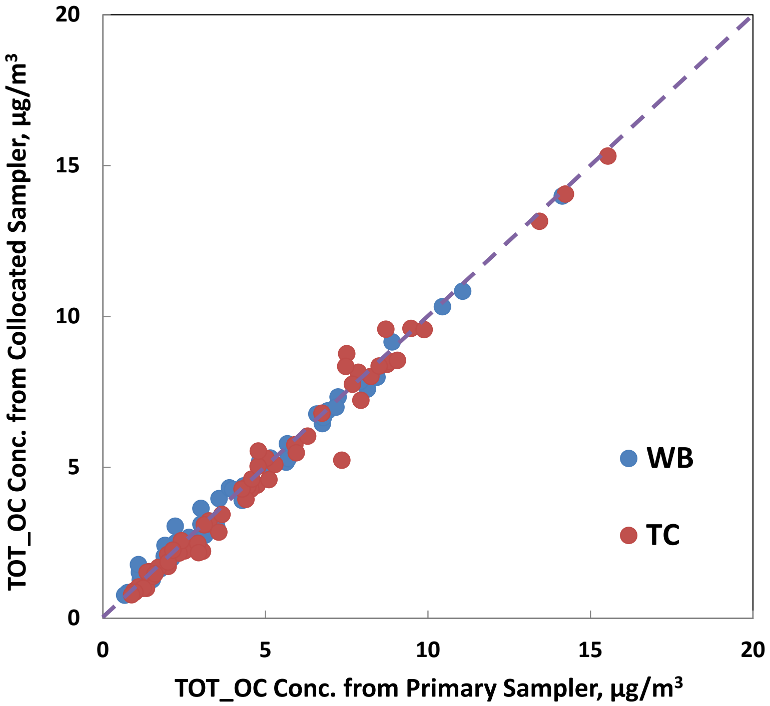


Figure 18. Collocated data for OC concentration by NIOSH_TOT method at WB and TC sites during 2014.

Table 24. Statistics analysis of collocated data for OC concentration by NIOSH_TOT method at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	118	120
Slope	0.967 (±0.013)	0.999 (±0.018)
Intercept	0.137 (±0.064)	-0.140 (±0.106)
R^2	0.990	0.982

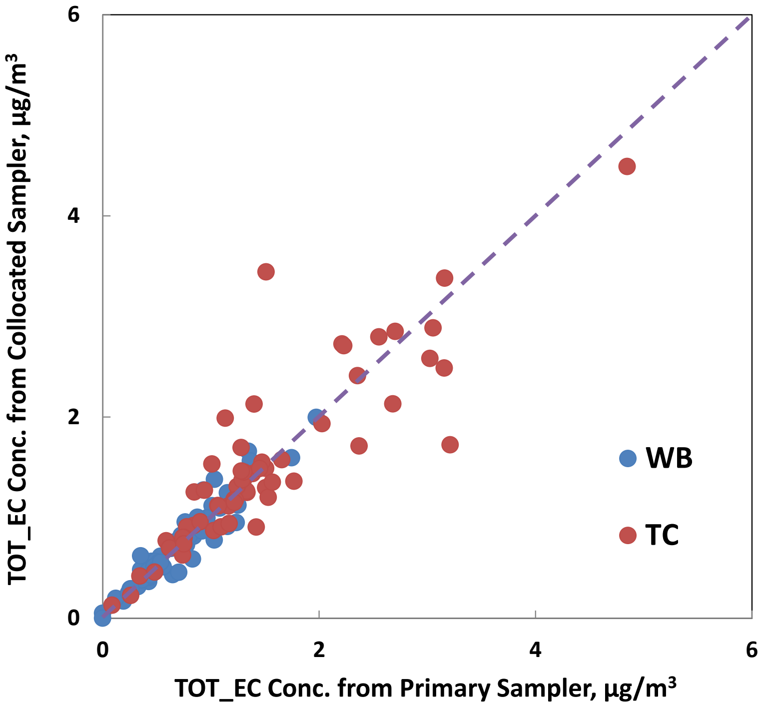


Figure 19. Collocated data for EC concentration by NIOSH_TOT method at WB and TC sites during 2014.

Table 25. Statistics analysis of collocated data for EC concentration by NIOSH_TOT method at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	114	120
Slope	0.980 (±0.048)	0.842 (±0.062)
Intercept	0.033 (±0.040)	0.256 (±0.107)
R^2	0.881	0.763

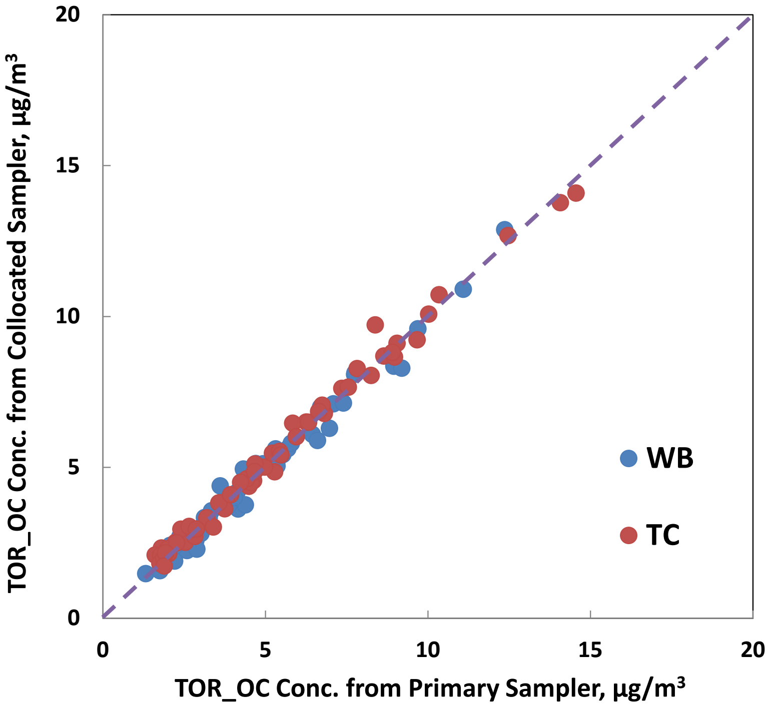


Figure 20. Collocated data for OC concentration by IMPROVE_A_TOR method at WB and TC sites during 2014.

Table 26. Statistics analysis of collocated data for OC concentration by IMPROVE_A_TOR method at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	120	122
Slope	1.00 (±0.018)	1.02 (±0.012)
Intercept	0.004 (±0.091)	-0.207 (±0.074)
R^2	0.982	0.992

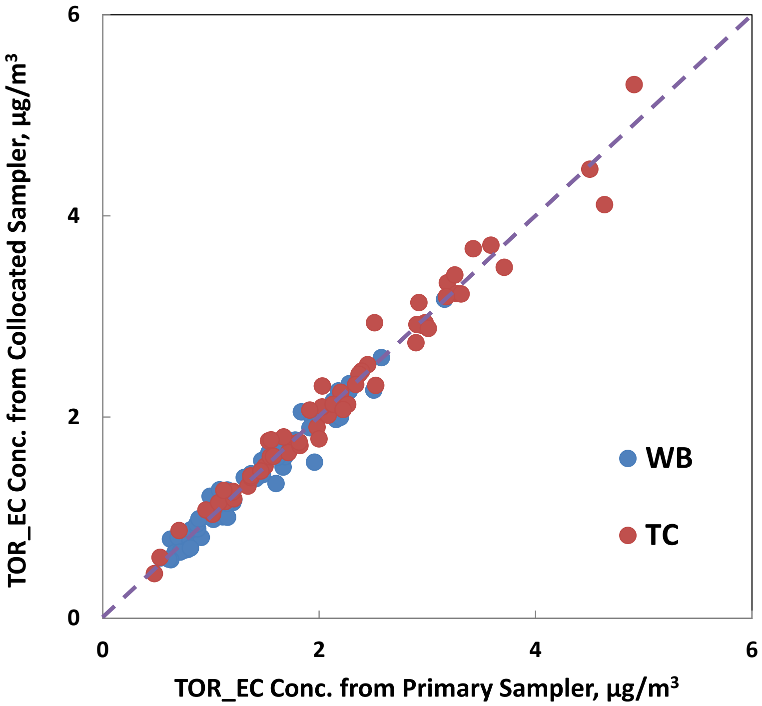


Figure 21. Collocated data for EC concentration by IMPROVE_A_TOR method at WB and TC sites during 2014.

Table 27. Statistics analysis of collocated data for EC concentration by IMPROVE_A_TOR method at WB and TC sites during 2014.

Statistics/Site	WB	TC
n	114	122
Slope	1.01 (±0.027)	1.00 (±0.018)
Intercept	0.004 (±0.040)	-0.021 (±0.045)
R^2	0.962	0.982

Bias and precisions were computed for collocated comparisons on $PM_{2.5}$ mass and select chemical species with the screened data set. The equations used are as below,

$$\overline{C_i} = \frac{X_i + Y_i}{2} \qquad (10)$$

$$\%RB_i = \frac{(Y_i - X_i)}{\overline{C_i}} \times 100\% \qquad (11)$$

$$\%\overline{RB} = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_i - X_i) \times 100\%}{\overline{C_i}} \qquad (12)$$

$$\%RSD = \frac{\left|\%RB_i\right|}{\sqrt{2}} \qquad (13)$$

$$\%\overline{RSD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\%RSD_i^2} \qquad (14)$$

Where:

X_i = ambient air concentration of sample i measured at sampler X, µg/m^3

Y_i = ambient air concentration of sample i measured at collocated sampler Y, µg/m^3

n = number of paired samples

%RB = percent relative bias

%RSD = percent relative standard deviation (precision)

The uncertainty values reported to HKEPD are summarized under the column titled “Avg. UNC” in Table 28. This is the average of all the relative uncertainties reported to HKEPD over the collocated data set and is calculated as follows,

$$\overline{UNC} = \frac{1}{n}\sum_{i}\sum_{j}\frac{UNC_{ij}}{CONC_{ij}} \qquad (15)$$

Where:

$CONC_{ij}$ = concentration for the i^th^ exposure with the j^th^ sampler (j = 1 or 2), µg/m^3

UNC_{ij} = uncertainty for the i^{th} exposure with the j^{th} sampler (j = 1 or 2), µg/m^3

n = total number of measurements

The column titled “UNC/RSD” is essentially the average under- or over-estimate of the uncertainty for each chemical species reported during 2014. Ratios greater than 200% or less than 50% indicate situations in which the uncertainties reported to HKEPD were different from the uncertainties estimated from collocated data by a factor of 2 or more. The column titled “Counts” shows the number of observations included in the averages subject to the criteria defined above.

Table 28. Average relative biases and average relative standard deviations (precisions) of concentrations of $PM_{2.5}$ mass and select chemical species for collocated samples.

	%RB	%RSD	Avg. UNC[1]	UNC/RSD[2]	Counts[3]
$PM_{2.5}$_Teflon	0.5%	1.2%	N/A	N/A	234
$PM_{2.5}$_QMA	-0.4%	3.5%	N/A	N/A	238
Na^+	3.1%	15.6%	24.6%	157.6%	242
NH_4^+	0.6%	10.8%	9.3%	85.9%	240
K^+	-0.1%	9.1%	34.2%	**375.0%**	204
NO_3^-	12.2%	25.0%	55.3%	**221.4%**	204
SO_4^{2-}	0.4%	4.4%	9.9%	**226.3%**	242
TOR_OC	1.9%	6.0%	13.9%	**232.8%**	242
TOR_EC	0.6%	5.7%	20.0%	**351.1%**	236
TOT_OC	1.9%	8.4%	16.5%	195.2%	238
TOT_EC	-2.7%	14.8%	29.3%	197.7%	235
Al	1.9%	6.4%	21.3%	**332.4%**	217
Si	2.6%	8.6%	13.5%	157.2%	230
P	0.7%	23.6%	36.2%	153.3%	219
S	-0.5%	3.3%	5.1%	157.2%	240
K	0.1%	3.2%	5.5%	172.3%	240
Ca	3.3%	6.4%	7.2%	111.5%	240
Ti	2.4%	13.9%	22.8%	164.6%	218
V	-1.0%	10.5%	11.5%	109.4%	240
Fe	2.9%	4.6%	7.5%	162.8%	240
Ni	-1.8%	15.0%	30.1%	**200.8%**	201
Cu	-3.1%	14.6%	17.6%	120.6%	204
Zn	-0.7%	4.7%	9.5%	**201.1%**	240
Br	2.0%	11.7%	18.0%	153.1%	182

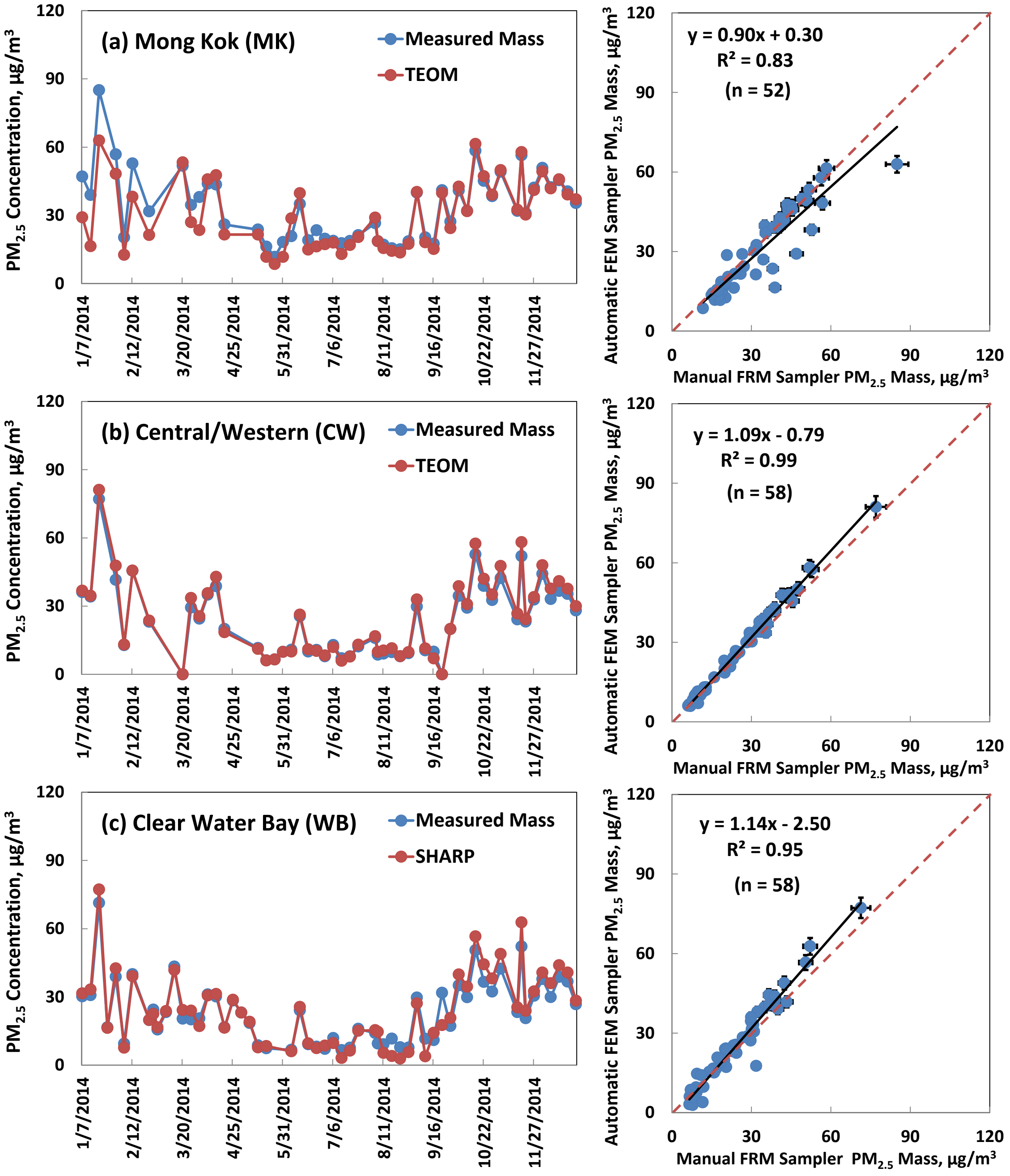
[1] Average value of the relative uncertainties as reported to HKEPD.

[2] UNC/RSD is the ratio of reported uncertainties divided by the uncertainty determined by collocated samples. Values greater than 200% or less than 50% are shown in bold.

[3] Counts are the number of individual observations included in the statistics. Only observations where both concentration values were above the 2×LOD were included.

3.3.7 $PM_{2.5}$ Mass Concentrations: Gravimetric vs. Continuous Measurements

Continuous monitoring of $PM_{2.5}$ concentrations were also conducted at all six monitoring sites. TEOMs (Tapered Element Oscillating Microbalance) are installed at MK, CW, TC, TW, and KC sites. At YL site, a Beta Attenuation Monitor (BAM-1020, Met One Instruments) was deployed for $PM_{2.5}$ monitoring since June 2013. At WB site, a Synchronized Hybrid Ambient Real-time Particulate Monitor (Model 5030 SHARP, Thermo Scientific) has been set up for continuous $PM_{2.5}$ monitoring since May 2011. At KC site, TEOM was replaced by a Model 602 Beta^{PLUS} Particle Measurement System (Teledyne-API), which has been conducting beta attenuation monitoring of ambient $PM_{2.5}$ concentrations since November 2014. Comparisons of $PM_{2.5}$ mass concentrations from gravimetric measurement and 24-hr average TEOM/beta gauge measurement were conducted. The results are presented in both time-series plots and scatter plots (Figure 22). Uncertainties of TEOM/beta gauge are assumed to be 5% of concentration. The two measurements show good agreement (R^2 = 0.82–0.99) with slopes ranging from 0.91 to 1.19.



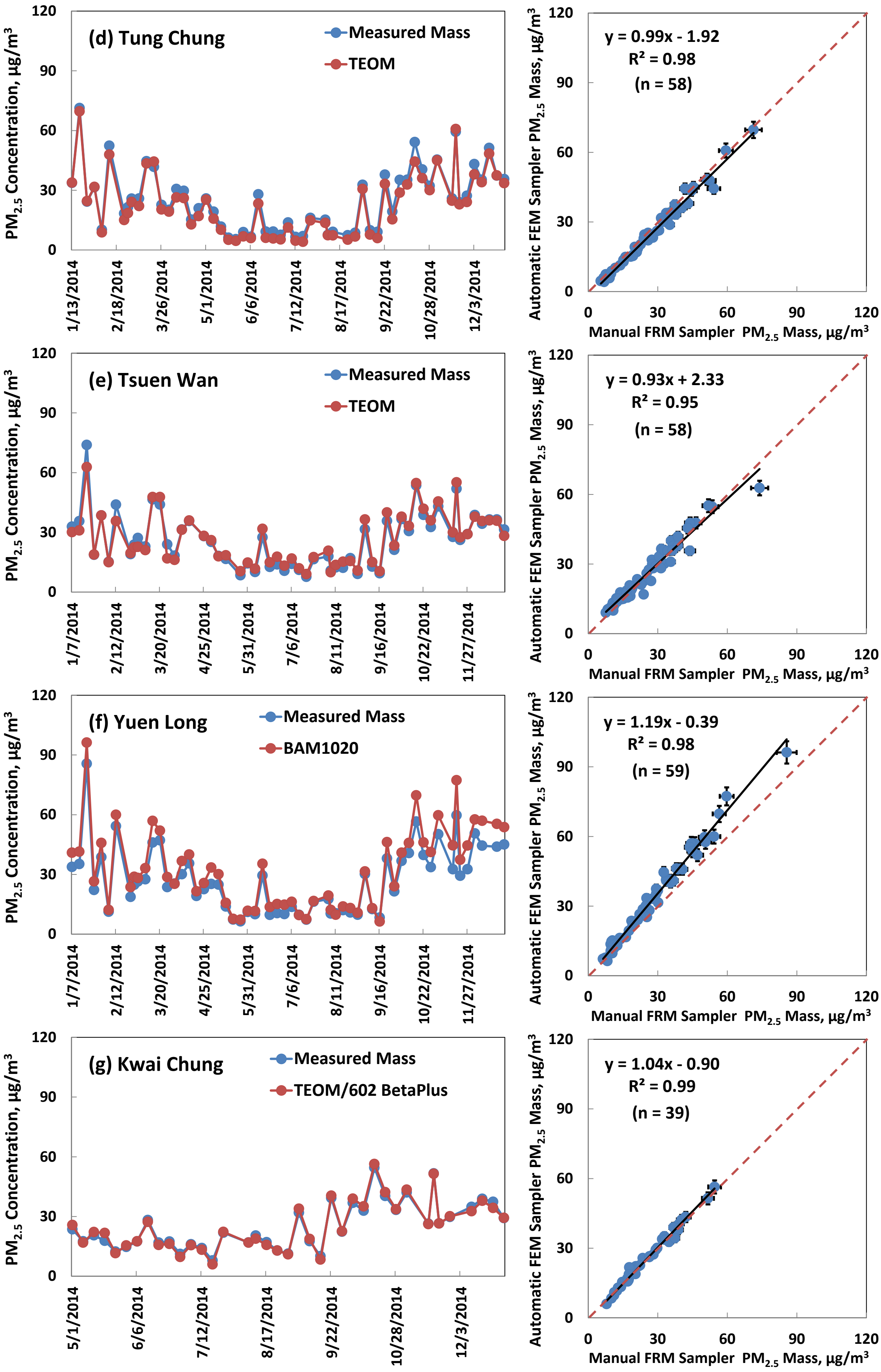


Figure 22. Comparisons of PM$_{2.5}$ mass concentrations from gravimetric and continuous measurements at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC.

4. Comparison of the $PM_{2.5}$ Sampling Campaigns in 2000–2001, 2004–2005, 2008–2009, 2011, 2012, 2013, and 2014

A side-by-side comparison of the seven one-year $PM_{2.5}$ monitoring studies is shown in Appendix A [Chow et al., 2002, 2006, 2010; Yu et al., 2012, 2013, 2014]. In this study, the $PM_{2.5}$ monitoring sites remained the same as those in the years of 2011–2013, while a seventh monitoring site, the KC AQMS, was added into the network in May 2014.

Compared to the year of 2013, the annual average $PM_{2.5}$ concentrations at MK, CW, WB, TC, TW, and YL sites in 2014 exhibited decreases of 7.7%, 11.1%, 11.3%, 11.7%, 11.2%, and 12.0%, respectively. Annual trends of $PM_{2.5}$ mass were examined for MK, CW, WB, TC, TW, and YL sites across the years when data are available (Figure 23). In general, the fine PM levels at all six sites have been decreasing since 2011.

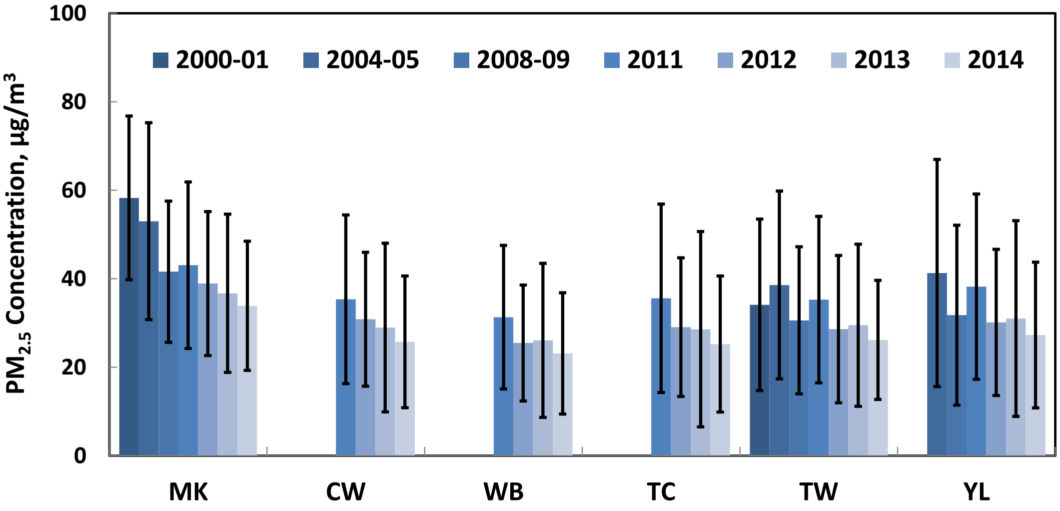
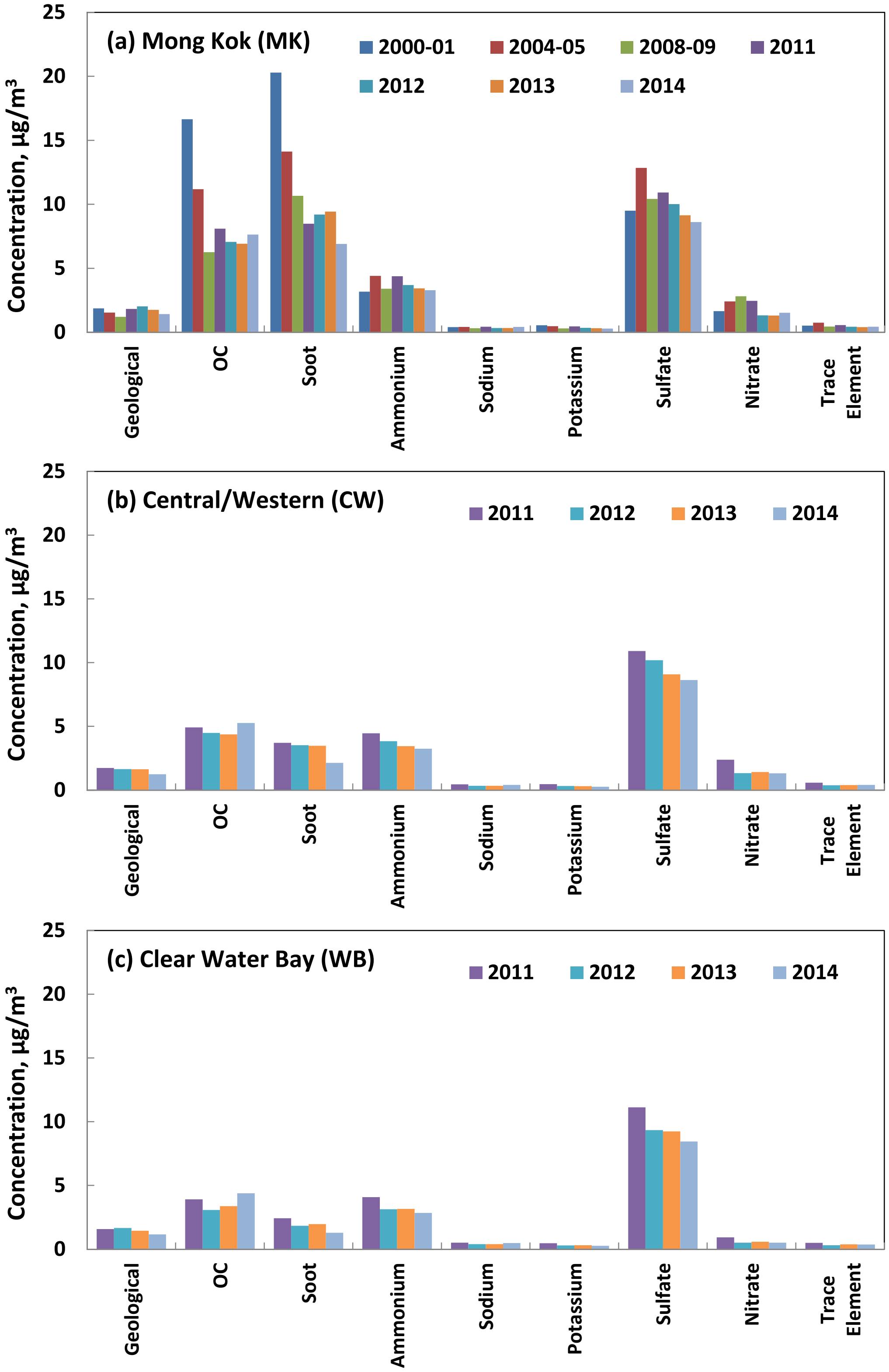


Figure 23. Comparisons of annual average $PM_{2.5}$ mass concentrations at MK, CW, WB, TC, TW, and YL sites from 2000 to 2014 (wherever data are available). The error bars represent standard deviations which are a function of the natural variability of the environmental levels and are not indicative of the analytical precision.

Measured species were grouped into six categories described in Section 3.3.5 for better comparison (Figure 24). For OC and EC at MK, TW, and YL sites, high concentration levels were observed in the first two studies (i.e. 2000–01 and 2004–05) and then the concentrations maintained at lower levels since 2008. At all six sites, the OC and EC levels were comparable during 2011–2014. For ammonium, sulfate, and nitrate, a quite clear decreasing trend could be observed across all six sites since 2011. For other species (i.e., geological material, ammonium, sodium, potassium, and non-crustal elements), the concentrations were at similar levels all over the years.


(a) Mong Kok (MK)
2000-01
2004-05
2008-09
2011
2012
2013
2014
(b) Central/Western (CW)
(c) Clear Water Bay (WB)
Concentration, µg/m³
0
5
10
15
20
25
Geological
OC
Soot
Ammonium
Sodium
Potassium
Sulfate
Nitrate
Trace Element

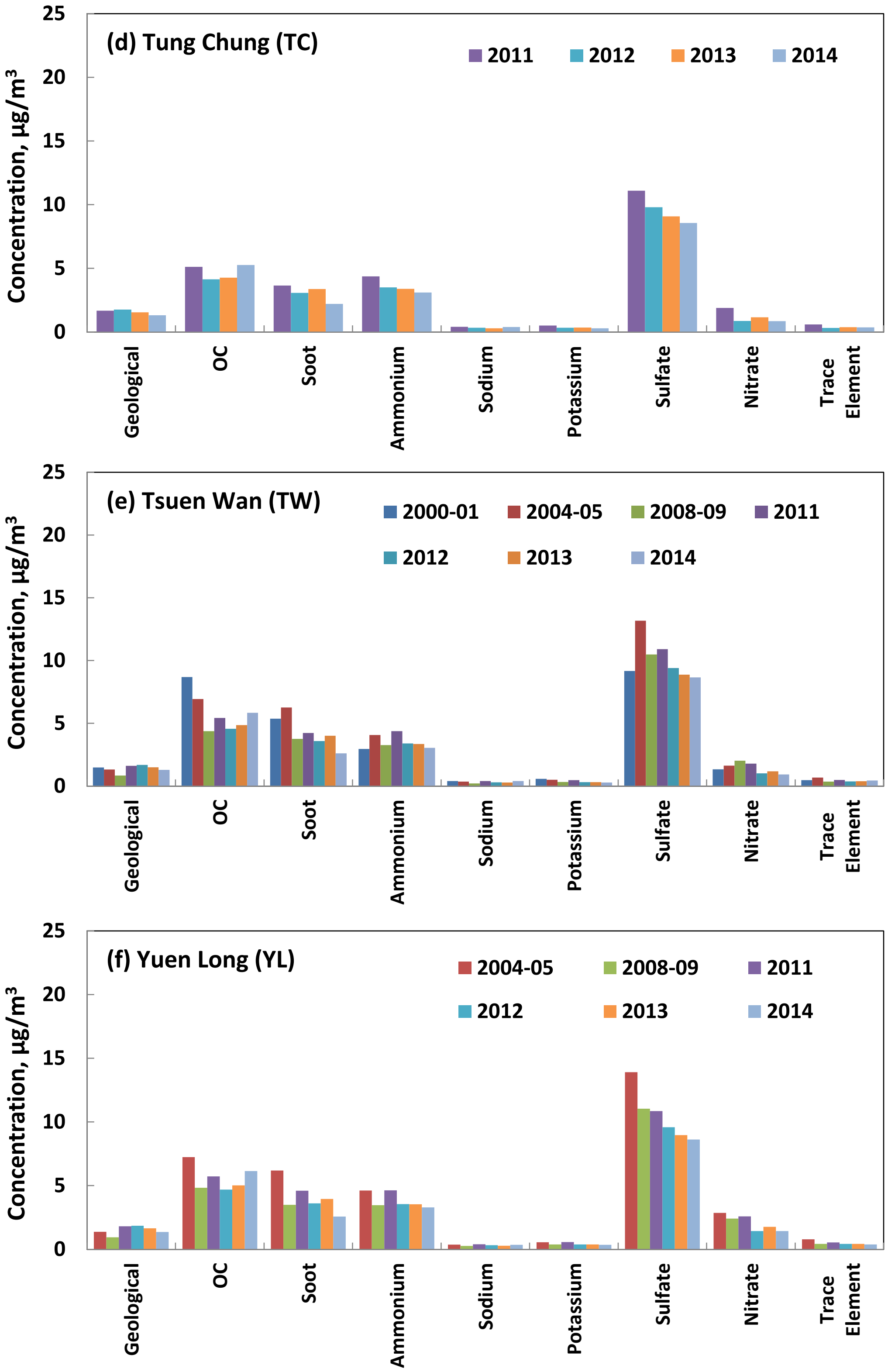


Figure 24. Annual trend of major components of $PM_{2.5}$ samples collected at (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, and (f) YL.

5. Summary

This data summary report covers the validation and quality assurance aspects of the chemical analysis of filter samples from the Hong Kong $PM_{2.5}$ speciation network from January 1 through December 31, 2014. Samplings were conducted at Mong Kok (MK), Central/Western (CW), Clear Water Bay (WB), Tung Chung (TC), Tsuen Wan (TW), and Yuen Long (YL) sites on a 1-in-6 day schedule which yielded a total of 60 sampling events through the year. A seventh sampling site, Kwai Chung (KC), was added into the network and started sampling in May 2014, yielding a total of 40 sampling events. Of the 1042 $PM_{2.5}$ filter samples received, 1034 $PM_{2.5}$ filter samples are considered valid after Level I data validation. Therefore, a total of 1156 filters (1034 $PM_{2.5}$ samples and 122 field blanks) were submitted for comprehensive chemical analyses.

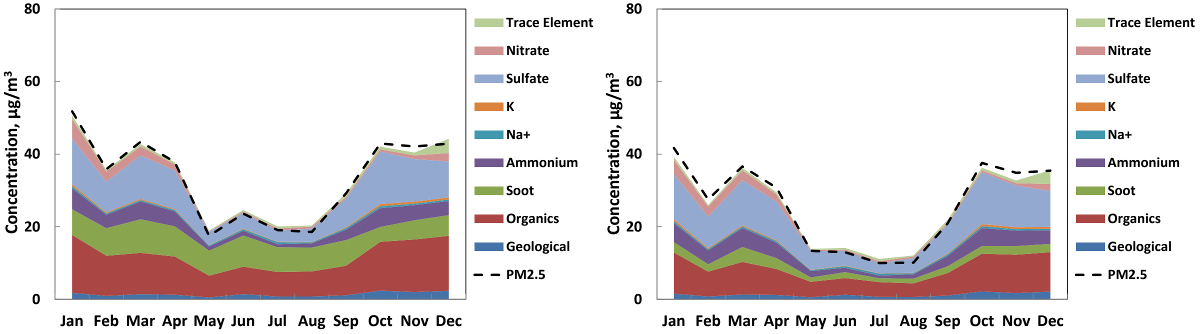
The valid data rate exceeds 99%. 8 filter samples (3 Teflon filters and 5 quartz fiber filters) were flagged as invalid during sampling quality assurance process. The laboratory accuracy and precision were within limits as demonstrated by routine QC samples.

The highest annual average $PM_{2.5}$ concentration of 33.90 $\mu g/m^3$ was measured at the roadside MK site. The lowest annual average $PM_{2.5}$ concentration of 23.12 $\mu g/m^3$ was found at the suburban WB site. The $PM_{2.5}$ concentrations at all the 7 monitoring sites were within the new AQO annual $PM_{2.5}$ standard of 35 $\mu g/m^3$.

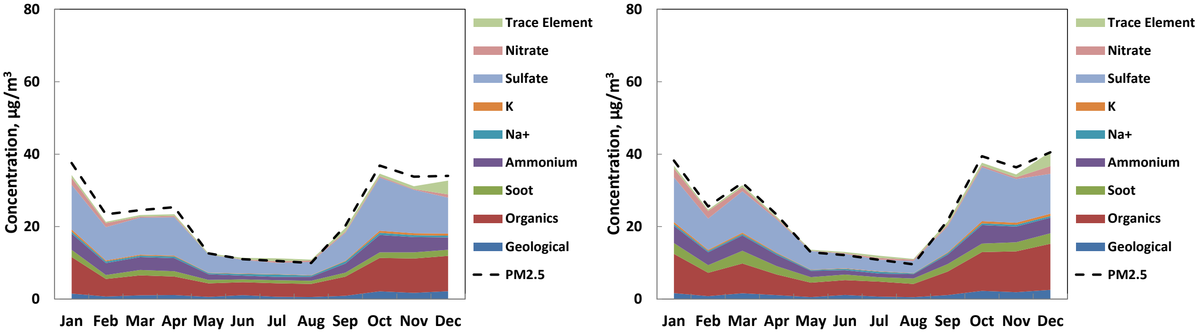
Two levels of validation were performed on the complete dataset. Reconstructed mass and measured mass were highly correlated with correlation coefficients (R^2) ranging from 0.97 to 0.99 at individual sites. It further supports the validity of both gravimetric analysis and chemical measurements. The reconstructed mass and the measured mass agreed excellently.

Similar to the past years, sulfate is still the most abundant component in the $PM_{2.5}$ across all the six sites (25.4–36.6%). Organic carbon is the second most abundant component with mass contributions ranging from 19.0% at WB site to 22.5% at MK and YL sites. It is noted that OC, instead of OM, is discussed here since the conversion factor between OM and OC is empirical and uncertain. Nitrate concentrations were much lower than those of sulfate, contributing 2.1–5.2% to the total fine PM mass at all the sites. Ammonium was reasonably balanced by sulfate and nitrate and it was suggested to exist dominantly as ammonium sulfate across all the sampling sites in the year of 2014. EC concentrations exhibited a clear roadside-urban-suburban gradient pattern with the highest concentration (6.91 $\mu gC/m^3$, 20.4% of the $PM_{2.5}$ mass) observed at MK site and the lowest concentration (1.29 $\mu gC/m^3$, 5.6% of the $PM_{2.5}$ mass) at WB site.

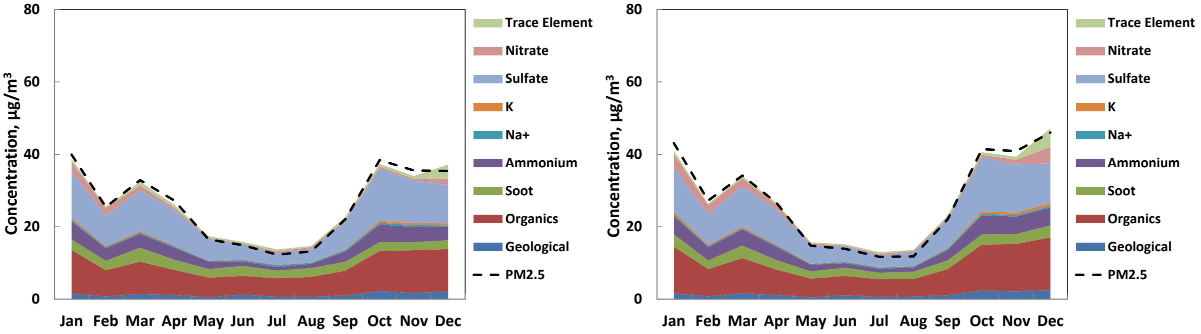
(a) Mong Kok (MK) **(b) Central/Western (CW)**



(c) Clear Water Bay (WB) **(d) Tung Chung (TC)**



(e) Tsuen Wan (TW) **(f) Yuen Long (YL)**



(g) Kwai Chung (KC)

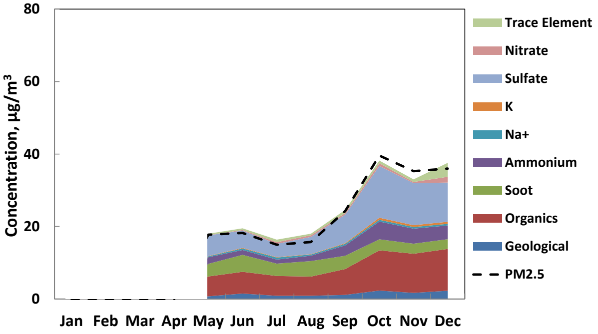


Figure 25. Monthly average of $PM_{2.5}$ mass concentrations and chemical compositions for (a) MK, (b) CW, (c) WB, (d) TC, (e) TW, (f) YL, and (g) KC during 2014 $PM_{2.5}$ speciation study.

Monthly average $PM_{2.5}$ concentration and chemical composition for individual sites are shown in Figure 25 in order to examine the seasonal trends of the $PM_{2.5}$ constituents. The results showed that Hong Kong experienced higher $PM_{2.5}$ levels during fall and winter months (Jan, Feb, Oct, Nov, and Dec) while summer months (Jun–Aug) usually have lower $PM_{2.5}$ concentrations.

The annual average concentrations of $PM_{2.5}$ mass and major constituents remained at similar levels to those in the past two years. The clear roadside-urban-suburban gradient pattern of

EC concentrations suggested that local sources (e.g. on-road vehicles) were its major contributors. While a wide range of measures taken by the HKSAR Government to control the vehicular emissions have proved to be effective and responsible for the general decreasing trend of EC levels observed at roadside, continuous efforts are needed to contain the air pollution at lower levels so as to keep compliance with the new AQO criteria.

References

Bevington, P. R. (1969), Data Reduction and Error Analysis for the Physical Sciences, MaGraw Hill, New York, NY.

Birch, M. E. and R. A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, 25, 221-241.

Chen, L. -W. A., J. C. Chow, J. G. Watson, H. Moosmüller, and W. P. Arnott (2004), Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis, *J. Aerosol Sci.*, 35, 765-780.

Chow, J. C., J. G. Watson, L. C. Pritchett, W. R. Pierson, C. A. Frazier, and R. G. Purcell (1993), The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U. S. air quality studies, *Atmos. Environ.*, 27A, 1185-1201.

Chow, J. C., J. G. Watson, L. -W. A. Chen, W. P. Arnott, H. Moosmüller, and K. K. Fung (2004), Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols, *Environ. Sci. Technol.*, 38, 4414-4422.

Chow J. C., J. G. Watson, L. -W. A. Chen, M. C. O. Chang, N. F. Robinson, D. Trimble, and S. D. Kohl (2007), The IMPROVE_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, *J. Air Waste Manage. Assoc.*, 57, 1014-1023.

Chow J. C., J. G. Watson, Kohl, S. D., Gonzi, M. P., L. -W. A. Chen (2002), Measurements and Validation for the Twelve Month Particulate Matter Study in Hong Kong, available at: http://www.epd.gov.hk/epd/english/environmentinhk/air/studyrpts/files/final_version_hkepdfinalreport_rev12-12-02.pdf.

Chow J. C., J. G. Watson, Kohl, S. D., Voepel, H. E., L. -W. A. Chen (2006), Measurements and Validation for the Twelve Month Particulate Matter Study in Hong Kong, available at: http://www.epd.gov.hk/epd/english/environmentinhk/air/studyrpts/files/HKEPDFinalReportRev_V8.pdf.

Chow J. C., J. G. Watson, Kohl, S. D., L. -W. A. Chen (2010), Measurements and validation of the 2008/2009 particulate matter study in Hong Kong, available at: http://www.epd.gov.hk/epd/english/environmentinhk/air/studyrpts/files/HKEPDFinalReportRev_11-29-10_v2.pdf.

Hong Kong Observatory (HKO) (2013), The year's weather – 2013, Climatological Publications, available at: http://www.weather.gov.hk/wxinfo/pastwx/ywx2013.htm.

Subramanian, R., A. Y. Khlystov, and A. L. Robinson (2006), Effect of peak inert-mode temperature on elemental carbon measured using thermal-optical analysis, *Aerosol Sci. Technol.*, 40, 763-780.

U. S. Environmental Protection Agency (USEPA) (1999), Particulate Matter ($PM_{2.5}$) Speciation Guidance, available at: http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/specfinl.pdf.

U. S. Environmental Protection Agency (USEPA) (2012), Quality Assurance Guidance Document for $PM_{2.5}$ Chemical Speciation Sampling at Trends, NCore, Supplemental and Tribal Sites, available at: http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/CSN_QAPP_v120_05-2012.pdf.

Watson, J. G., J. C. Chow, and C. A. Frazier (1999), X-ray fluorescence analysis of ambient air samples, Elemental Analysis of Airborne Particles, Vol 1, by S. Landsberger and M. Creatchman, Eds. Gordon and Breach Science, Amsterdam, 67-96.

Watson, J. G., B. J. Turpin, and J. C. Chow (2001), The measurement process: Precision, accuracy, and validity, in *Air Sampling Instrument for Evaluation for Atmospheric Contaminants*, 9th ed., B. S. Cohen and C. S. J. McCammon, Eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 201-216.

Witz, S., R. W. Eden, M. W. Wadley, C. Dunwoody, R. P. Papa, and K. J. Torre (1990), Rapid loss of particulate nitrate, chloride and ammonium on quartz fiber filters during storage, *J. Air Waste Manage. Assoc.*, 40, 53-61.

Yu, J. Z., X. H. H. Huang, and W. M. Ng (2012), Final report for provision of service for fine particulate matter (PM2.5) sample chemical analysis, available at: http://www.epd.gov.hk/epd/english/environmentinhk/air/studyrpts/files/final_report_mvtmpms_2011.pdf.

Yu, J. Z., X. H. H. Huang, and W. M. Ng (2013), Final report for provision of service for fine particulate matter (PM2.5) sample chemical analysis, available at: http://www.epd.gov.hk/epd/english/environmentinhk/air/studyrpts/files/final_report_mvtmpms_2012.pdf.

Yu, J. Z., X. H. H. Huang, T. Zhang, and W. M. Ng (2014), Final report for chemical speciation of $PM_{2.5}$ filter samples, January 1 through December 31, 2013, available at: http://www.epd.gov.hk/epd/sites/default/files/epd/english/environmentinhk/air/studyrpts/files/final_report_mvtmpms_2013.pdf.

Appendix A. Side-by-side comparison of the seven one-year studies of $PM_{2.5}$ samples (in µg/m^3) collected during 2000–01, 2004–05, 2008–09, 2011, 2012, 2013, and the current 2014 period. Carbon concentrations (in µgC/m^3) are from the IMPROVE_TOR method.

	2001	2001	2001	2005	2005	2005	2005	2009	2009	2009	2009	2011	2011	2011	2011	2011	2011	2012	2012	2012	2012	2012	2012	2013	2013	2013	2013	2013	2013	2014	2014	2014	2014	2014	2014
	MK	TW	HT	MK	TW	YL	HT	MK	TW	YL	HT	MK	CW	WB	TC	TW	YL	MK	CW	WB	TC	TW	YL	MK	CW	WB	TC	TW	YL	MK	CW	WB	TC	TW	YL
Teflon Mass	58.28	34.12	23.66	53.02	38.59	41.31	28.44	41.60	30.61	31.78	24.10	43.08	35.36	31.32	35.57	35.30	38.22	38.93	30.87	25.48	29.07	28.64	30.15	36.72	28.99	26.08	28.59	29.50	31.01	33.90	25.75	23.12	25.25	26.19	27.29
QMA Mass	62.50	37.28	25.85	54.87	40.75	43.91	29.64	45.92	34.00	36.34	25.94	47.92	39.84	35.89	39.81	40.56	42.89	58.03	49.44	45.58	46.96	48.26	50.23	41.38	33.36	30.38	32.40	33.97	35.37	35.99	27.68	23.81	27.37	28.66	29.80
Cl^-	0.256	0.138	0.143	0.283	0.126	0.264	0.124	0.312	0.175	0.213	0.298	0.205	0.191	0.105	0.109	0.122	0.174	0.10	0.12	0.07	0.07	0.08	0.13	0.119	0.137	0.093	0.093	0.095	0.111	0.203	0.178	0.123	0.123	0.138	0.142
NO_3^-	1.65	1.34	0.71	2.40	1.64	2.86	0.76	2.81	2.03	2.42	1.51	2.45	2.39	0.93	1.90	1.80	2.59	1.32	1.33	0.51	0.87	1.01	1.43	1.31	1.42	0.58	1.16	1.17	1.76	1.53	1.32	0.52	0.87	0.93	1.43
SO_4^{2-}	9.50	9.17	8.64	12.84	13.17	13.91	11.91	10.41	10.48	11.04	9.66	10.91	10.91	11.13	11.09	10.91	10.85	10.01	10.19	9.34	9.80	9.41	9.58	9.14	9.08	9.25	9.08	8.88	8.96	8.60	8.64	8.45	8.56	8.66	8.63
NH_4^+	3.17	2.96	2.16	4.40	4.07	4.62	3.06	3.40	3.27	3.47	2.63	4.37	4.45	4.09	4.38	4.38	4.63	3.68	3.85	3.13	3.50	3.40	3.56	3.42	3.45	3.16	3.40	3.36	3.54	3.28	3.25	2.85	3.10	3.05	3.29
Na^+	0.398	0.397	0.679	0.423	0.362	0.375	0.527	0.320	0.211	0.262	0.380	0.431	0.452	0.510	0.413	0.404	0.402	0.32	0.34	0.39	0.34	0.31	0.32	0.326	0.342	0.401	0.299	0.292	0.278	0.420	0.415	0.482	0.397	0.398	0.352
K^+	0.457	0.492	0.403	0.479	0.486	0.562	0.433	0.278	0.308	0.365	0.259	0.467	0.463	0.483	0.534	0.492	0.590	0.35	0.34	0.29	0.34	0.32	0.37	0.319	0.314	0.318	0.350	0.309	0.385	0.286	0.271	0.273	0.297	0.294	0.348
OC	16.64	8.69	4.23	11.18	6.93	7.23	3.92	6.26	4.38	4.83	2.70	8.09	4.92	3.91	5.13	5.44	5.73	7.05	4.49	3.07	4.14	4.57	4.69	6.92	4.37	3.37	4.27	4.86	5.02	7.64	5.27	4.39	5.26	5.83	6.15
EC	20.29	5.37	1.68	14.12	6.26	6.19	2.28	10.66	3.76	3.49	1.21	8.48	3.71	2.43	3.65	4.24	4.61	9.20	3.52	1.84	3.07	3.59	3.60	9.42	3.48	1.96	3.37	4.01	3.96	6.91	2.15	1.29	2.22	2.61	2.57
TC	36.91	14.04	5.89	25.28	13.18	13.42	6.19	16.91	8.12	8.31	3.89	16.55	8.60	6.31	8.76	9.65	10.31	16.25	8.01	4.92	7.21	8.16	8.29	16.33	7.84	5.33	7.64	8.86	8.97	14.54	7.41	5.68	7.48	8.45	8.72
Al	0.1139	0.1146	0.1094	0.1408	0.1414	0.1448	0.1223	0.0986	0.0828	0.0913	0.0828	0.1942	0.2008	0.1990	0.2009	0.1910	0.2114	0.2365	0.2134	0.2260	0.2322	0.2118	0.2368	0.2034	0.2054	0.2005	0.2061	0.1916	0.2115	0.1671	0.1656	0.1686	0.1774	0.1676	0.1784
Si	0.4778	0.3870	0.3489	0.3469	0.3141	0.3221	0.2546	0.2485	0.1853	0.2073	0.1685	0.3981	0.4209	0.3980	0.4079	0.3888	0.4349	0.4393	0.3882	0.4064	0.4175	0.3899	0.4311	0.3732	0.3897	0.3527	0.3604	0.3436	0.3779	0.2760	0.2703	0.2690	0.2902	0.2728	0.2897
P	0.0092	0.0050	0.0028	0.1886	0.1950	0.1917	0.1747	0.0225	0.0237	0.0229	0.0225	0.0194	0.0163	0.0150	0.0158	0.0163	0.0155	0.0211	0.0144	0.0129	0.0140	0.0138	0.0148	0.0177	0.0133	0.0124	0.0121	0.0140	0.0145	0.0188	0.0153	0.0134	0.0160	0.0157	0.0137
S	3.4886	3.3789	3.0534	4.3005	4.5835	4.5622	4.2099	3.3471	3.4305	3.4535	3.1650	3.6677	3.7263	3.8399	3.7518	3.7641	3.7813	3.3455	3.4259	3.1763	3.3431	3.1509	3.2280	3.1377	3.1135	3.2338	3.1359	3.1369	3.0990	3.0873	3.0814	3.0280	3.1124	3.0678	3.0908
Cl	0.1169	0.0874	0.1432	0.1391	0.0758	0.1590	0.0709	0.1037	0.0568	0.0941	0.0799	0.0889	0.1203	0.0720	0.0726	0.0640	0.0774	0.0386	0.0566	0.0235	0.0373	0.0491	0.0621	0.0754	0.0909	0.0954	0.0861	0.0741	0.0788	0.1303	0.1322	0.1324	0.1023	0.0947	0.0941
K	0.5517	0.5858	0.4892	0.4678	0.5080	0.5631	0.4551	0.3064	0.3281	0.3828	0.2780	0.4619	0.4677	0.4740	0.5192	0.4797	0.5722	0.3447	0.3324	0.3005	0.3454	0.3211	0.3882	0.3658	0.3714	0.3690	0.3931	0.3622	0.4366	0.3136	0.2943	0.3030	0.3298	0.3194	0.3839
Ca	0.1705	0.1262	0.1024	0.1082	0.0896	0.0891	0.0652	0.1102	0.0729	0.0738	0.0626	0.1298	0.1209	0.0914	0.0959	0.1006	0.1111	0.1461	0.1072	0.1090	0.1117	0.1253	0.1207	0.1244	0.1088	0.0853	0.0968	0.1053	0.1088	0.1061	0.0891	0.0722	0.0830	0.0993	0.0935
Ti	0.0092	0.0088	0.0079	0.0109	0.0102	0.0114	0.0062	0.0109	0.0084	0.0097	0.0062	0.0128	0.0118	0.0106	0.0138	0.0117	0.0156	0.0147	0.0124	0.0116	0.0147	0.0127	0.0153	0.0126	0.0116	0.0103	0.0128	0.0106	0.0139	0.0099	0.0085	0.0078	0.0099	0.0093	0.0108
V	0.0134	0.0137	0.0117	0.0190	0.0237	0.0195	0.0167	0.0175	0.0182	0.0144	0.0177	0.0146	0.0150	0.0119	0.0139	0.0206	0.0139	0.0197	0.0182	0.0133	0.0140	0.0208	0.0145	0.0219	0.0190	0.0145	0.0143	0.0245	0.0142	0.0263	0.0232	0.0148	0.0158	0.0258	0.0176
Cr	0.0010	0.0009	0.0006	0.0017	0.0015	0.0017	0.0014	0.0014	0.0012	0.0016	0.0011	0.0021	0.0020	0.0022	0.0022	0.0021	0.0024	0.0023	0.0022	0.0019	0.0022	0.0022	0.0022	0.0022	0.0018	0.0017	0.0021	0.0017	0.0020	0.0021	0.0019	0.0018	0.0021	0.0021	0.0023
Mn	0.0128	0.0124	0.0077	0.0170	0.0158	0.0170	0.0123	0.0127	0.0113	0.0127	0.0087	0.0214	0.0214	0.0174	0.0226	0.0186	0.0215	0.0194	0.0168	0.0132	0.0158	0.0163	0.0190	0.0163	0.0168	0.0130	0.0152	0.0156	0.0183	0.0132	0.0130	0.0103	0.0128	0.0155	0.0140
Fe	0.2692	0.1871	0.1219	0.2579	0.1858	0.1996	0.1190	0.2343	0.1325	0.1552	0.0947	0.2958	0.1978	0.1582	0.2094	0.1932	0.2215	0.3051	0.1881	0.1527	0.1959	0.1962	0.2223	0.2779	0.1818	0.1344	0.1777	0.1780	0.2027	0.2538	0.1585	0.1207	0.1707	0.1802	0.1877
Co	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0002	0.0002	0.0002	0.0001	0.0002	0.0005	0.0005	0.0003	0.0004	0.0003	0.0004	0.0002	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0000	0.0001	0.0000	0.0007	0.0004	0.0002	0.0003	0.0002	0.0003
Ni	0.0055	0.0054	0.0047	0.0061	0.0071	0.0068	0.0050	0.0049	0.0052	0.0044	0.0050	0.0050	0.0050	0.0042	0.0048	0.0064	0.0049	0.0065	0.0060	0.0045	0.0048	0.0113	0.0051	0.0068	0.0062	0.0052	0.0051	0.0073	0.0049	0.0070	0.0063	0.0042	0.0045	0.0068	0.0051
Cu	0.0113	0.0090	0.0052	0.0110	0.0104	0.0113	0.0065	0.0210	0.0188	0.0167	0.0169	0.0252	0.0215	0.0225	0.0226	0.0207	0.0234	0.0214	0.0181	0.0177	0.0157	0.0151	0.0167	0.0230	0.0182	0.0203	0.0248	0.0212	0.0378	0.0217	0.0142	0.0159	0.0237	0.0182	0.0321
Zn	0.1794	0.1743	0.1087	0.2399	0.2186	0.2381	0.1727	0.1579	0.1343	0.1600	0.1177	0.2156	0.2364	0.1948	0.2909	0.1936	0.2188	0.1887	0.1598	0.1337	0.1366	0.1704	0.1879	0.1567	0.1452	0.1397	0.1301	0.1501	0.1515	0.1347	0.1311	0.1062	0.1134	0.2017	0.1183
Ga	0.0004	0.0004	0.0005	0.0018	0.0030	0.0024	0.0026	0.0003	0.0004	0.0003	0.0004	0.0003	0.0002	0.0002	0.0002	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001	0.0000	0.0002	0.0000	0.0002	0.0002	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0000
As	0.0046	0.0055	0.0042	0.0053	0.0063	0.0084	0.0043	0.0012	0.0010	0.0016	0.0006	0.0043	0.0046	0.0053	0.0050	0.0046	0.0058	0.0030	0.0036	0.0026	0.0032	0.0029	0.0029	0.0035	0.0037	0.0040	0.0042	0.0038	0.0044	0.0019	0.0024	0.0023	0.0023	0.0020	0.0022
Se	0.0021	0.0022	0.0020	0.0003	0.0004	0.0005	0.0004	0.0003	0.0004	0.0004	0.0006	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Br	0.0129	0.0127	0.0121	0.0106	0.0099	0.0116	0.0108	0.0172	0.0148	0.0143	0.0174	0.0172	0.0170	0.0190	0.0159	0.0156	0.0171	0.0132	0.0134	0.0160	0.0115	0.0108	0.0122	0.0129	0.0133	0.0158	0.0133	0.0128	0.0133	0.0132	0.0127	0.0144	0.0125	0.0115	0.0123
Rb	0.0036	0.0043	0.0032	0.0020	0.0025	0.0029	0.0019	0.0010	0.0011	0.0015	0.0008	0.0011	0.0013	0.0014	0.0015	0.0014	0.0016	0.0007	0.0008	0.0006	0.0009	0.0006	0.0010	0.0007	0.0006	0.0005	0.0009	0.0006	0.0008	0.0000	0.0001	0.0001	0.0003	0.0003	0.0005
Sr	0.0013	0.0011	0.0011	0.0011	0.0011	0.0015	0.0015	0.0017	0.0019	0.0020	0.0015	0.0030	0.0032	0.0030	0.0027	0.0029	0.0030	0.0018	0.0015	0.0016	0.0016	0.0015	0.0014	0.0020	0.0018	0.0020	0.0018	0.0015	0.0017	0.0008	0.0006	0.0007	0.0010	0.0007	0.0006
Y	0.0001	0.0001	0.0002	0.0004	0.0004	0.0004	0.0003	0.0003	0.0004	0.0003	0.0004	0.0002	0.0002	0.0004	0.0002	0.0003	0.0004	0.0001	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0000	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Zr	0.0006	0.0006	0.0005	0.0016	0.0013	0.0007	0.0010	0.0010	0.0008	0.0011	0.0010	0.0006	0.0002	0.0003	0.0004	0.0004	0.0006	0.0014	0.0008	0.0006	0.0008	0.0005	0.0007	0.0004	0.0005	0.0006	0.0008	0.0007	0.0006	0.0005	0.0007	0.0006	0.0006	0.0008	0.0011
Mo	0.0005	0.0005	0.0007	0.0015	0.0011	0.0017	0.0012	0.0007	0.0006	0.0007	0.0005	0.0016	0.0012	0.0011	0.0011	0.0013	0.0009	0.0001	0.0000	0.0001	0.0001	0.0002	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0021	0.0018	0.0014	0.0024	0.0018	0.0027
Pd	0.0012	0.0017	0.0011	0.0019	0.0014	0.0016	0.0020	0.0006	0.0007	0.0008	0.0005	0.0016	0.0018	0.0023	0.0021	0.0019	0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0001	0.0001
Ag	0.0011	0.0017	0.0014	0.0013	0.0020	0.0018	0.0012	0.0010	0.0007	0.0008	0.0007	0.0003	0.0002	0.0003	0.0002	0.0001	0.0001	0.0000	0.0006	0.0003	0.0003	0.0004	0.0002	0.0003	0.0003	0.0002	0.0004	0.0002	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Cd	0.0019	0.0023	0.0022	0.0022	0.0021	0.0025	0.0018	0.0008	0.0007	0.0007	0.0005	0.0006	0.0005	0.0005	0.0006	0.0004	0.0007	0.0007	0.0013	0.0007	0.0004	0.0010	0.0008	0.0002	0.0006	0.0005	0.0008	0.0006	0.0004	0.0005	0.0003	0.0001	0.0005	0.0001	0.0005
In	0.0018	0.0020	0.0014	0.0009	0.0010	0.0017	0.0011	0.0005	0.0005	0.0005	0.0005	0.0003	0.0003	0.0005	0.0006	0.0003	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000
Sn	0.0188	0.0203	0.0116	0.0131	0.0188	0.0162	0.0084	0.0107	0.0101	0.0100	0.0091	0.0131	0.0122	0.0125	0.0135	0.0120	0.0154	0.0041	0.0038	0.0035	0.0052	0.0032	0.0049	0.0034	0.0045	0.0046	0.0061	0.0059	0.0113	0.0032	0.0038	0.0038	0.0041	0.0055	0.0076
Sb	0.0046	0.0049	0.0038	0.0042	0.0027	0.0039	0.0033	0.0009	0.0009	0.0014	0.0015	0.0080	0.0074	0.0068	0.0075	0.0067	0.0087	0.0005	0.0005	0.0007	0.0007	0.0002	0.0004	0.0005	0.0011	0.0006	0.0004	0.0007	0.0009	0.0021	0.0018	0.0015	0.0019	0.0003	0.0021
Ba	0.0267	0.0170	0.0086	0.0106	0.0081	0.0068	0.0053	0.0031	0.0031	0.0024	0.0026	0.0167	0.0108	0.0087	0.0104	0.0101	0.0108	0.0348	0.0101	0.0127	0.0108	0.0115	0.0205	0.0109	0.0066	0.0048	0.0048	0.0060	0.0119	0.0042	0.0041	0.0039	0.0041	0.0045	0.0056
La	0.0131	0.0087	0.0130	0.0105	0.0081	0.0082	0.0112	0.0036	0.0034	0.0040	0.0053	0.0164	0.0156	0.0146	0.0163	0.0132	0.0165	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0040	0.0040	0.0041	0.0043	0.0042	0.0061
Au	0.0003	0.0005	0.0004	0.0003	0.0006	0.0002	0.0003	0.0000	0.0000	0.0001	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0001	0.0002	0.0002	0.0001	0.0002	0.0002	0.0001	0.0000	0.0001	0.0002	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001
Hg	0.0001	0.0002	0.0001	0.0000	0.0003	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Tl	0.0001	0.0001	0.0001	0.0002	0.0001	0.0000	0.0003	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0001	0.0002	0.0002	0.0000	0.0001	0.0001
Pb	0.0664	0.0726	0.0576	0.0478	0.0498	0.0624	0.0432	0.0405	0.0406	0.0437	0.0399	0.0597	0.0604	0.0626	0.0630	0.0599	0.0671	0.0399	0.0397	0.0370	0.0365	0.0346	0.0384	0.0383	0.0394	0.0413	0.0421	0.0374	0.0428	0.0317	0.0313	0.0344	0.0346	0.0312	0.0356
U	0.0001	0.0002	0.0002	0.0013	0.0011	0.0017	0.0018	0.0008	0.0007	0.0007	0.0010	0.0040	0.0035	0.0040	0.0038	0.0038	0.0035	0.0001	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002	0.0002	0.0005	0.0000	0.0001