

## **TECHNICAL ANNEX 2**

### **RSP Monitoring Exercise**

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## 1. BACKGROUND

- 1.1.1 All samplers and equipment used in the monitoring exercise were properly calibrated and methodologies employed are traceable to the Mainland or international recognised standards. Methodologies used by the EPD or published by USEPA were used for the collection and analysis of the RSP samples in PRDEZ.
- 1.1.2 When the existing EPD and USEPA standards were not fully covered for any particular procedures of this monitoring exercise, worldwide-established monitoring methods were referenced to and modified to suit specific requirements.
- 1.1.3 Measurement and analysis for RSP followed the "Quality Assurance Handbook for Air Pollution Measurement System, Section 2.11 Reference Method for the Determination of Particular Matter as RSP in the Atmosphere (High Volume RSP Method) {USEPA ref: EPA-600/R-94/038b dated April 1994}" issued by the USEPA.
- 1.1.4 An independent audit including pilot tests had been conducted by Dr. Judith Chow of Worldwide Environmental Corporation in March 2000 before the program started. Any potential procedures leading to unacceptable performance of the sampling and analysis program had been identified. The recommended modifications had been taken into account as far as technically feasible during the actual sampling and analysis exercise to ensure the quality of result.

## 2. FIELD SAMPLING METHODOLOGY

### 2.1 Location of Sampling Points

#### PRDEZ

- 2.1.1 Eight sampling points in the PRDEZ as shown in Figure 2-1 have been identified for the RSP sampling. All the sampling points are selected because they are potentially influenced by industrial, urban, motor vehicle, rural emissions as listed in Table 2-1 and also they provide good representation of those emission sources.
- 2.1.2 For security and accessibility purpose, sampling locations of the monitoring exercise were collocated with the existing air quality monitoring stations operated by the Guangdong Environmental Protection Bureau, if the station met the monitoring requirements of this study.
- 2.1.3 Locations of the sampling points were inspected prior to the monitoring exercise to determine their suitability for the study. The following section provided a brief description of the selected sampling locations:

#### S1. Shenzhen City Nanshan District 深圳市南山區 - Industrial

Nanshan District is located to the west of Shenzhen City of approximately 17 km and it is a heavy industry district in the PRDEZ. Industrial operations with different scales such as power station, quarry and domestic electric product factory etc. can be found in this area. The monitoring station was set up at the rooftop of the Lixiang Secondary School, which is also a regular monitoring station operated by Shenzhen EPB.

#### S2. Dongguan City Changping Town 東莞市常平鎮 - Industrial

Changping Town is located at the east of Dongguan City of approximately 25 km. Major industries in this town are bleaching and dyeing, and textiles, both of which involving heat treatment. There are totally 36 management districts scattering around the urban area of Changping Town and all industrial factories are evenly distributed in these management districts. The RSP monitoring station was located at the rooftop of the City Government Building, which is situated in the centre of this town.

#### S3. Zengcheng City Xiancun Town 增城市仙村鎮 - Industrial

Zengcheng City is located at the east side of Guangzhou City of approximately 47 km, an area filled with low-grade cement manufacturing operations. Xiancun Town is one of the largest

cement suppliers in Zengcheng City and it is located along the Guangshen Railway Line. The RSP monitoring station was set up at the rooftop of the City Government Building due to its central location.

S4. Guangzhou City Guang-shen Highway (Shahe Section) 廣州市北環高速公路 (沙河路段) - Mobile

Guangshen Highway is one of the major access roads connecting Guangzhou City and other cities in the PRDEZ. Located at the sub-rural area of Guangzhou, the Guang-shen Highway Shahe Section is merged with another high traffic flow road network, Guang-shan Highway. The RSP sampling location at this interchange reflected the characteristic of typical mobile emission sources in the PRDEZ.

S5. Guangzhou City Baiyuan District 廣州市白雲區 - Urban

Luhu Park is one of regular air quality monitoring stations of Guangzhou City. The park is located at the northern side of the Guangzhou City, which is a relatively clean area. In where low density office buildings and residential blocks surround the park.

S6. Guangzhou City Conghua City 廣州市從化市 - Rural

Conghua City is located to the far north of Guangzhou City of approximately 74 km and it is remote away from any urbanised areas in the PRDEZ. Given its remote location and unpolluted environment, the city is selected for the background RSP monitoring.

S7. Jiangmen City Fengjiang District 江門市蓬江區 - Industrial

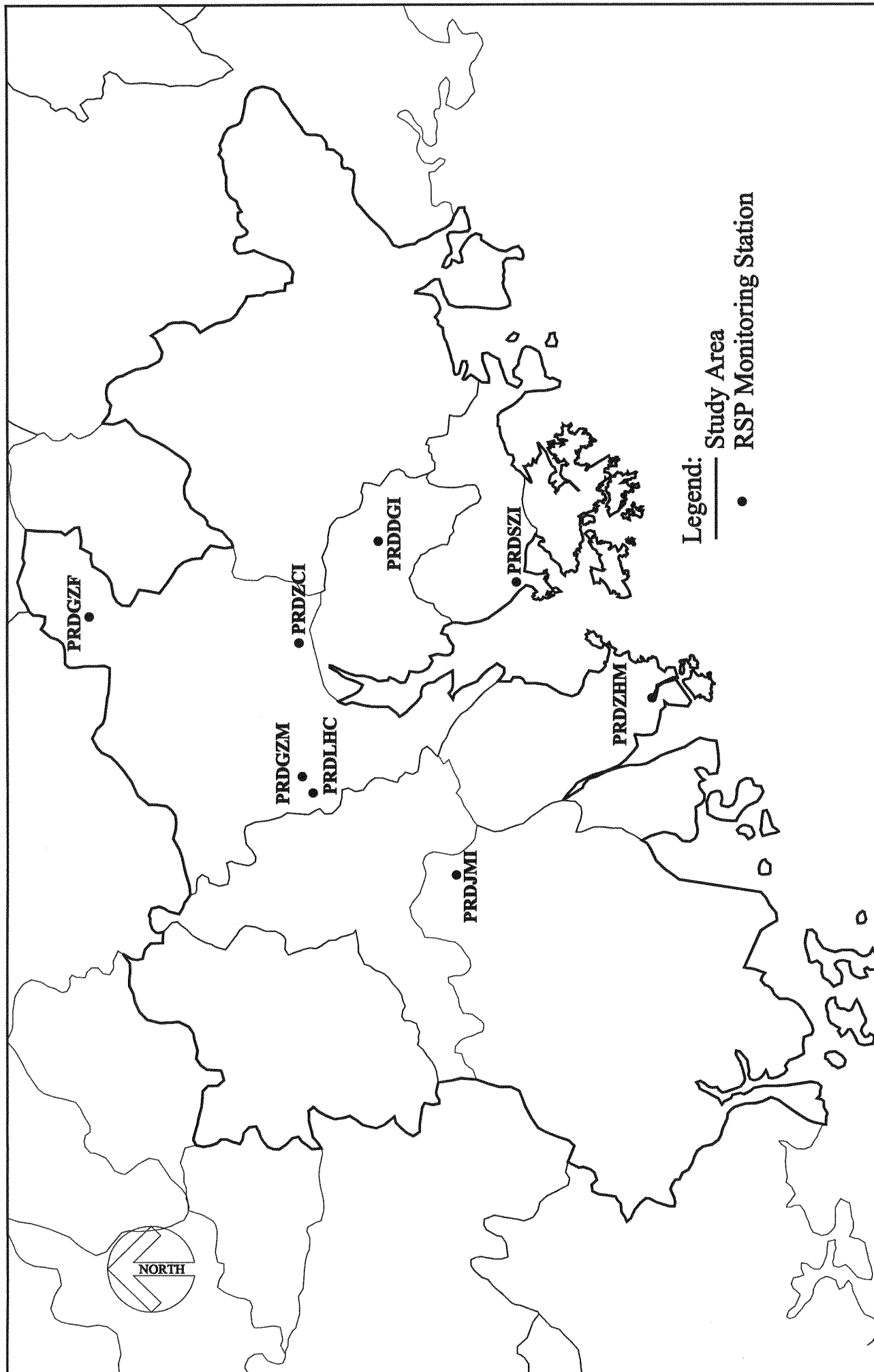
Jiangmen City is located at the west side of the PRDEZ. Industries in Jiangmen City are mainly light industries such as papermaking, sugar production, chemical and food etc. Nearly all industries are located at the sub-urban area close to Jiangmen River. An existing monitoring station at Beijie is operated by Jiangmen EPB for industrial emission sampling.


S8. Zhuhai /Zhongshan City Guang-zhu Highway (Sanxiang Section) 珠海/中山市廣珠高速公路 (三鄉鎮路段) - Mobile

Apart from Guangshen Highway, Guangzhu Highway is another major highway in the PRDEZ for RSP sampling. A new section of the Guangzhu Highway was just completed for increasing the traffic capacity to Zhuhai. The new section of the highway merged with the old Guangzhu Highway at Sanxiang and the peak traffic flow is at this intersection.

Table 2-1 Location of the RSP Monitoring Stations

No.	Sample Label	Station Label	City/ Town	Monitoring Station	Site Characteristics	Distance from Source (m)	Probe Sampling Height (ab ground lev)
S1	PRDSZI	Nanshan (Industry)	Shenzhen City Nanshan District 深圳市南山區 (工業源)	EPB Monitoring Station at Lixiang Secondary School	Industrial: Mixed industrial/ residential	NA	~ 14 m
S2	PRDDGI	Changping (Urban)	Dongguan City Changping Town 東莞市常平鎮 (工業源)	City Government Building	Industrial: Mixed industrial/ residential	NA	~ 16 m
S3	PRDZCI	Xiancun (Industry)	Zengcheng City Xiancun Town 廣州市增城市 (工業源)	City Government Building	Industrial: Mixed industrial/ residential	NA	~ 8 m
S4	PRDGZM	Guang-shen (Mobile)	Guangzhou City Guang-shen Highway 廣州市北環高速公路 (交通源)	Building close to Shahe section of Guangshen Highway	Mobile: Residential	~5m	~ 18 m
S5	PRDLHC	Guangzhou (Urban)	Guangzhou City Baiyuan District 廣州市白雲區 (城市源)	Luhu Park	Urban: Mixed commercial/ residential	NA	~ 8 m
S6	PRDGZF	Conghua (Rural)	Guangzhou City Conghua City 廣州市從化市 (郊區)	Upper Reservoir Dam of Chunen Power Station,	Rural: Background	NA	~ 5 m
S7	PRDJMI	Jiangmen (Industry)	Jiangmen City Fengjiang District 江門市蓬江區 (工業源)	EPB Monitoring Station at Beijie, Jiangmen City	Industrial: Mixed industrial/ residential	NA	~ 9 m
S8	PRDZHM	Guangzhu (Mobile)	Zhuhai/Zhongshan City Guang-zhu Highway 珠海/中山市 (廣珠高速公路三鄉鎮路段) (交通源)	Building close to the Sanxiang section of the Guangzhu Highway	Mobile: Residential	~10m	~ 15 m



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	Title: Locations of the RSP Monitoring Stations in the Pearl River Delta Region			
	Figure: 2-1	Scale: NTS	Page No: TA2-3	

## 2.2 RSP Sampling Period

- 2.2.1 Two months was allowed for the organisation of the monitoring team and selection of the suitable monitoring locations after studying the existing available air quality data in Region.
- 2.2.2 120 RSP samples were monitored in a six-day cycle with a temporal resolution of 24 hours, coincide with the EPD's RSP sampling programme in HKSAR. The sampling was commenced at the end of December 1999 when the start of the meteorological period producing peak RSP concentrations in HKSAR and PRDEZ. The monitoring programme was suspended during the Chinese New Year Holiday and the field sampling of the whole monitoring exercise completed in May 2000.

## 2.3 Field Sampling Methodology and Procedure

- 2.3.1 All samplers and equipment used in the monitoring exercise were properly calibrated. All methodologies employed are traceable to national or internationally recognised standards. These include methods used by the EPD, and those published by the United States Environmental Protection Agency (USEPA).

### High Volume Sampler

- 2.3.2 A high-volume RSP sampler was used to draw a known volume of ambient air, at constant flow rate, through a size-selective inlet onto filter paper. Particulates in the RSP size range were then collected on the filter during the specified 24-hr sampling period.

### Filter Handling

- 2.3.3 8" x 10" QMA quartz filter paper was employed for the sampling exercise. Prior to use, all filter papers were checked for any possible sign of contamination, pinholes, tears or other defects that would rule out their use. Care was taken to ensure the filters were not folded or damaged in any way during delivery, sampling or collection.
- 2.3.4 Filter papers were pre-weighed before field sampling. After pre-weighing, the filters were contained in a dry, dust-free cabinet with desiccators. The filters were then placed in sealed plastic bags for delivery to the sampling station, and were delivered back to the laboratory after sampling. Details of the sampling dates and station names were clearly labelled.

### Siting of the Sampling Equipment

- 2.3.5 The selection criteria for the collection of RSP followed that issued by USEPA, Section 8 of Appendix E to Part 58, 40 CFR Chapter I (July 1999 edition) - *Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring and the Quality Assurance and Technical Specifications on the Monitoring of Ambient Air and Emission (Trial)* issued by the State Monitoring Center.

## 2.4 Quality Control and Quality Assurance

### Quality Control on equipments and instrument

- 2.4.1 All equipment and instruments used in calibration, and routine sampling, were documented and traceable to Mainland or international primary standards. Regular maintenance was performed for all the samplers with calibrations being carried out and the schedule is listed in Table 2-2.

### Laboratory Analysis QA/QC Procedures

- 2.4.2 Quality control and assurance programme for the sampling and analysis of RSP is presented. The programme is comparable with quality procedures currently used by HKEPD, USEPA and the HK Government Laboratories. An independent audit including pilot tests had been conducted by Dr. Judith Chow of Worldwide Environmental Corporation in March 2000 before the programme was started. The recommended modifications been taken into account as far as technically feasible during the monitoring exercise. Key modifications are presented in Table 2-3.

Table 2-2 Frequencies of the Calibration and Equipment Maintenance

Calibration Requirement	Frequency
general inspection	every sampling
General cleaning	every sampling
stability of flow rate	every sampling
Temperature	every sampling
flow rate	every month
Leakage	every quarter
Clock	every quarter
timer	every sampling
air volume	every sampling
RSP Concentration ( $\mu\text{g}/\text{m}^3$ )	Frequency of Cleaning
40	6 month (30 sampling days)
75	3 month (15 sampling days)
150	two month (10 sampling days)
200	one month (5 sampling days)
300	two weeks (2 sampling days)
>300	every occurrence

Table 2-3 Key Modifications of Sampling and Analysis Exercise

Filter Extraction	Implementation
Avoid manual trimming and Shredding of filters.	√
Reduce the extraction volume.	√
Modify the cleaning procedure for Erlenmeyer flasks.	√
Extract and analyse a separate portion of the filter for 10 % of samples	√
Anion Analysis	Implementation
Use the same calibration concentration levels for all ionic species within the same concentration level.	√
Evaluate nitrate retention times with spiked samples or by checking with the calibration standards immediately after the sample run.	√
Cation Analysis	Implementation
Interlaboratory comparisons necessary to ensure the validity of measurement.	√
Water soluble sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) should be quantified	√
Elemental Analysis	Implementation
Analyse the same metals by multiple metal analysis methods for the study.	√
Field Sample Audit	Implementation
Install a bug screen on sample inlet.	√
Clean and regrease the inlet at least every week.	√
Connect a flexible duct at the exhaust of the PM10 sampler with the other end downwind of the sampler.	√

√= Corresponding recommendations had been implemented by the monitoring exercise

- 2.4.3 The QA/QC programme includes sample labelling, chain of custody, field data recording, sampler calibration and calibration checks, sampler operational checks (e.g., leak testing), periodic sampling, collection and analysis of field blank samples, analytical instrument calibration, collocated sample analysis, and analysis of external standards.
- 2.4.4 A unique identification code was assigned to each sample to indicate monitoring location, pollutant type, and date and time of sample.
- 2.4.5 Approximately 10% field blanks of total samples were collected and sent back to laboratory for mass weighing and analysis. Field blanks included Metal Element Content in the Blank Filter, Anion Content in the Blank Filter, Ammonium Content in the Blank Filter and Weight of Particulate in the Blank Filter. All the results are insignificant as compared to the actual sample result. This demonstrated that the collected samples were not contaminated throughout the handling and transportation process.
- 2.4.6 Field blank and collocated samples were collected as part of the QA/QC procedures for the RSP monitoring programme. All field blank and collocated sample analyses showed satisfactory QA/QC performance within the pre-set requirements.

Limitations and Constraints of QA/QC

- 2.4.7 Apart from field blanks, approximately 10% collocated samples were collected and analysed. Due to the constraint of logistic arrangement of sampler and the constraint of electricity power supply in specific sampling locations, only two sampling locations which are Guangzhou City (Luhu Park) and Guangzhou City (Guangshen Highway Shahe Section) were selected for collecting collocated samples and field blanks samples.

Data Validation

- 2.4.8 Four data validation procedures were performed for screening all the sample data presented in this report.
- Relative Percentage Difference (RPD) of collocated samples - The control limits of RPD of collocated samples are not more than 20 %. (Criterion A)
  - Field Blank Samples results – The field blank sample results must be insignificant to the actual sample results. (Criterion B)
  - Detection Limits - The sample results presented must be higher than the respective analytical detection limits. (Criterion C)
  - Statistical Analysis – USEPA approved statistical method will be adopted to screen for outliers in the whole data sets. (Criterion D)
- 2.4.9 The Relative Percentage Difference of collocated samples is calculated by the following equation. The control limit of RPD is not more than 20 %. Most of the sample data sets complied with the control limit. Field blank sample results are all insignificant to the actual sample data.
- $$RPD = \{[A - \text{Average}(A, B)] / [\text{Average}(A, B)]\} * 100\% \quad \text{where } A, B = \text{Data of Sample \& Duplicate}$$
- 2.4.10 For samples which are not detected above detection limit, the concentrations of the respective sample will be presented as smaller than detection limits. The corresponding data set will be highlighted and discarded.
- 2.4.11 Statistical analyses including visual inspection of scattered plots for each tested parameter at each sampling station were performed. Suspected outliers were further tested with Discordance Test and Rosner's Test in accordance with the Guidance for Data Quality Assessment by the USEPA. (Ref: EPA/600/R-96/084, July 2000)
- 2.4.12 For data which do not pass any one of the above listed criteria, the data will be highlighted and discarded for presentation. The percentages of validation of all the individual sample data sets are above 90%. Results are presented in Table 3-1 and Table 3-2.

### 3. LABORATORY ANALYTICAL METHODOLOGY

#### 3.1 Mass Weighing

- 3.1.1 Procedures for mass weighing of the filter papers followed the procedures "Appendix J to Part 50 - Reference Method for the Determination of Particulate Matter as RSP in the Atmosphere". The filter was weighed before and after the sampling in a laboratory with a balance under controlled temperature and relative humidity. Both clean and sampled filters were conditioned for 24 hours continuously at a constant temperature between 20°C and 30°C and at a constant relative humidity between 30% and 40% before weight.
- 3.1.2 After mass weighing of the filter paper, the filter paper was divided into four equal portions. Three portions were used for the analysis of the inorganic and organic species. The remaining portion was archived and kept at low temperature as sampling record until the completion of the study.



Table 3-1 Percentage of Validation of Sample Data of the Monitoring Exercise

RSP		No. of Data Screened	Data Not Meeting Criterion A	Data Not Meeting Criterion B	Data Not Meeting Criterion C	Data Not Meeting Criterion D	Validated Data	% of Validation
Ion Analysis	F <sup>-</sup>	123	0	0	0	4	119	96.7
	Cl <sup>-</sup>	123	0	0	0	3	120	97.6
	Br <sup>-</sup>	123	0	0	0	2	121	98.4
	NO <sub>3</sub> <sup>-</sup>	123	0	0	0	2	121	98.4
	SO <sub>4</sub> <sup>2-</sup>	123	0	0	0	0	123	100.0
	NH <sub>4</sub> <sup>+</sup>	123	0	0	0	3	120	97.6
	Be	123	0	0	0	4	119	96.7
	Al	123	0	0	0	3	120	97.6
	V	123	0	0	0	2	121	98.4
	Cr	123	0	0	0	4	119	96.7
	Mn	123	0	0	0	4	119	96.7
	Ni	123	0	0	0	2	121	98.4
	Cu	123	2	0	0	4	117	95.1
	Zn	123	0	0	0	0	123	100.0
	Cd	123	0	0	0	6	117	95.1
	Ba	123	0	0	0	2	121	98.4
	Pb	123	0	0	0	4	119	96.7
	Hg	123	0	0	0	4	119	96.7
	As	123	0	0	0	4	119	96.7
	Fe	123	0	0	0	2	121	98.4
	Na <sup>+</sup>	123	0	0	0	3	120	97.6
	K <sup>+</sup>	123	0	0	2	5	116	94.3
Mg <sup>2+</sup>	123	0	0	7	4	112	91.1	
Ca <sup>2+</sup>	123	0	0	1	3	119	96.7	
MW		171	0	0	0	2	169	98.8
CA	OC	123	0	0	0	2	121	98.4
	EC	123	0	0	0	2	121	98.4
	TC	123	0	0	0	2	121	98.4

MW = Mass Weighing; CA = Carbon Analysis

Table 3-2 Summary of the Quality Control Exercise

RSP	No. of Sample Data	No. of Data Screened	Average No of Validated Data	Average % of Validation
Ion Analysis	123	123	119	96.7
Mass Weighing	171	171	169	98.8
Carbon Analysis	123	123	121	98.4

### 3.2 Elemental and Soluble Ion Analysis

3.2.1 In the original plan for the air quality monitoring exercise, metals, metal ions and halogens (Na<sup>+</sup>, K<sup>+</sup>, Br<sup>-</sup>, As, Be, Cd, Ni, Pb, Cr, Al, Mn, Fe, Ca, Mg, V, Zn, Ba, Cu, Hg) were analysed by inductively coupled plasma with mass spectroscopy (ICP/MS) while water soluble ions such as sulphate, ammonium, nitrate and chloride were quantified by ion chromatography.

3.2.2 Due to the complexity of this project, a combination of Mainland and United States laboratory analysis procedures had been employed for the elemental and soluble ions analysed as listed below. Table 3-3 listed the laboratory methods used for the analysis with the detection limit for each method.

- GB 13580.5-92: Determination of fluoride, chloride, nitrite, nitrate, sulphate in the wet precipitation - Ion chromatography
- GB 11911-89: Water quality - Determination of iron and manganese - Flame atomic absorption spectrometric method
- GB 11904-89: Water quality - Determination of potassium and sodium - Flame atomic absorption spectrophotometry
- GB 7479-87: Water quality - Determination of ammonium Nessler's reagent calorimetric method

- v. USEPA Method 3005A: Acid digestion of waters for total recoverable or dissolved metals for analysis by FAA or ICP spectroscopy
  - vi. USEPA Method 6020: Inductively Coupled Plasma - mass spectroscopy
  - vii. GPEMC In-house Method: Analysis of arsenic and mercury in RSP sampled paper - HG-AFS
- 3.2.3 All of these international analytical methods had been studied for its appropriate applications in this study by an independent reviewer and concluded that the application of these methods is suitable for the purpose. Moreover, by using analytical methodologies that are commonly applied in the Study area with equivalent technical acceptability, the accuracy of the analytical exercise could be much guaranteed.

### 3.3 Carbon Analysis

- 3.3.1 Quantification of elemental carbon and organic carbon on quartz fibre paper deposit was performed by Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocols. The Thermal Optical Reflectance method was also employed in addition to IMPROVE. Details of the methods are in accordance with the standard operation procedures from Desert Research Institute (DRI) (Ref: SOP#2-2046, June 2000), who had performed the carbon analysis for this sampling exercise.

Table 3-3 Method for the Ion Analysis and its Detection Limit

Ion	Analytical Method	Detection Limit ( $\mu\text{g}/\text{m}^3$ )
Al	ICP-MS	0.08
Ba	ICP-MS	0.003
Cd	ICP-MS	0.001
Cr	ICP-MS	0.03
Cu	ICP-MS	0.008
Mg	ICP-MS	0.06
Mn	ICP-MS	0.005
Ni	ICP-MS	0.005
Zn	ICP-MS	0.008
Pb	ICP-MS	0.005
V	ICP-MS	$7 \times 10^{-5}$
Be	ICP-MS	$5 \times 10^{-5}$
F <sup>-</sup>	IC	0.03
SO <sub>4</sub> <sup>2-</sup>	IC	0.05
Cl <sup>-</sup>	IC	0.03
NO <sub>3</sub> <sup>-</sup>	IC	0.04
Br <sup>-</sup>	IC	0.04
NH <sub>4</sub> <sup>+</sup>	Nessler's	0.05
Fe	AA	0.01
Ca	AA	0.02
K <sup>+</sup>	AA	$4 \times 10^{-5}$
Na <sup>+</sup>	AA	$5 \times 10^{-4}$
As	HG-AFS	$7 \times 10^{-5}$
Hg	HG-AFS	$1 \times 10^{-5}/5 \times 10^{-6}$
Remark	For the samples from Conghua and Luhua Park, 1/8 portion of filter paper was used for Hg analysis of which the detection limit is $5 \times 10^{-6} \mu\text{g}/\text{m}^3$ For the samples from other six sites, 1/16 portion of filter paper was used for Hg analysis of which the detection limit is $1 \times 10^{-5} \mu\text{g}/\text{m}^3$	