

APPENDIX 5

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SYSTEM AUDIT REPORT

**STUDY PLAN EVALUATION FOR
CHARACTERIZATION OF PM_{2.5} COMPOSITION
IN HONG KONG**

Tender Reference AS00-170
Inception Report

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1. PROJECT DESIGN

1.1 Project Plans

The reviewed project plans were: 1) Proposed Sampling and Analytical Work Plan for an Ad-hoc Study on the Composition of PM_{2.5}; and 2) Tender for the Provision of 12-month Service for the Operation and Maintenance of two Toxic Air Pollution (TAP) monitoring stations and two Temporary Toxic Air Pollutants Monitoring Stations. The first incorporates the second as a needed complement that includes gas as well as particle components.

The basic concept for these studies is good. However, a more detailed program plan is needed that integrates separate components from these plans, provides detail on the species to be measured and the methods applied, and the uses of the measurements. This integrated plan should include the following components: 1) a clear statement of project objectives; 2) a summary of findings from previous aerosol studies; 3) specific hypotheses to be tested by the monitoring; 4) a listing of the specific chemicals to be quantified and comparison of anticipated concentrations to instrumental detection limits, sampling schedules, and sample compositing to attain detection limits; 5) a summary of sampling and analytical methods and potential deviations from standard operating procedures; 6) measurement evaluation methods (including results of quality assurance (QA) and quality control (QC) tests and intercomparisons); 7) data analysis methods to test hypotheses; and 8) allocation of available resources to the different tasks. Data base naming conventions, units, structures, and software also need to be specified. The creation of this plan should involve all of the project participants, including those in the field, the laboratory staff, the data management staff, and the data interpretation staff.

1.2 Study Objectives

Since this is the first attempt at a comprehensive year-long PM_{2.5} aerosol characterization study, project objectives should not be too ambitious. The following objectives are realistic:

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

It is possible to add objectives, but they should be realistically obtainable within the scope of the measurement program.

1.3 Technical Approach

The technical approach appears adequate to accomplish the above-stated objectives, but it is probably not sufficient for all objectives that every interest group might desire. For example, without corresponding measurements of Hong Kong source emissions, quantitative source apportionment will not be possible within the context of this study. As noted above, this study can give some indication of contributing source types and help to design a cost-effective source characterization study to complement the ambient study. In future studies, concurrent 5 min to 1 hour duration measurements of wind speed, wind direction, temperature, and relative humidity at transport and urban sites will add value to the data interpretation.

2. SAMPLING SITES

Four sampling sites in the Hong Kong/Kowloon regions were visited on December 6, 2000. These stations are intended to represent concentrations in industrial, commercial, residential, and regional environments. All sites meet siting criteria for their intended purposes. There are no major obstructions or emissions sources within 2 m of the sampler inlets and spacing between samplers is sufficient to preclude flow interferences.

The written site surveys are good. They should specify the map datum for the coordinates so that GPS measurements will match with maps to be used for locating them. NAD-83 is becoming the worldwide standard, but there are historical Hong Kong datums that might be more appropriate for topographical maps. UTM coordinates and zones should also be reported so that distances between sites can be calculated. The types of nearby industries should provide greater detail about their products and fuel use.

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

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

The Hok Tsui (HT) site was also established in November, 2000 to represent regional concentrations at Hong Kong's southwest boundary. Marine aerosol and cargo ship emissions from the South China Sea are the predominant local sources. Transport is typically from the

continent during winter and from the ocean during summer, and there are probably diurnal variations in flows associated with sea/land breezes. Sampling probes are on a concrete platform located on a hillside ~60 m above mean sea level.

3. MEASUREMENT METHODS

3.1 Sampling

The following methods are applied in this study:

- Volatile organic Compounds (VOCs) with the Xontec Model 910A canister sampler followed by GC analysis according to U.S. EPA Method TO-14A.
- Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) with an Andersen GPS1X PUF sampler followed by solvent extraction and GC/MS analysis according to U.S. EPA method TO-9A.
- Polycyclic aromatic hydrocarbons (PAHs) sampled with an Andersen GPS1X PUF sampler followed by solvent extraction and GC/MS analysis according to U.S. EPA method TO-13.
- Polychlorinated biphenyls (PCBs) with a GPS1X PUF sampler followed by solvent extraction and GC/MS analysis according to the U.S. EPA TO-4 method.
- Carbonyls with a Xontec 925 sampler on silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) followed by extraction and HPLC analysis according to the U.S. EPA TO-11A method.
- Hexavalent chromium with a Xontec 920 filter sampler on bicarbonate impregnated filters followed by extraction and ion chromatographic analysis by California Air Resources Board's 039 method.
- PM_{2.5} mass, elements, ions, carbon, and solvent extractable organics sampled with an R&P 2025 Partisol sampler on Teflon and quartz filters followed by gravimetric, x-ray fluorescence, anion chromatography, automated colorimetry, atomic absorption spectrophotometry, thermal/optical reflectance combustion, and GC/MS according to laboratory-specific analysis procedures.

The sampling methods and procedures are well established and are widely applied in many U.S. compliance networks, the Photochemical Assessment Monitoring Stations (PAMS), and research networks. Special precautions that need to be taken are:

- Canister VOC sampling: PAMS usually samples for a few hours, and the pre-cleaned and evacuated 6L canisters are optimized for this period. The 24-hour sample duration in this project requires careful maintenance of the 10 mL/min flow rate throughout the 24-hour period. Leak checks should be performed on fittings and

valves before and after each sample. Flow rates should also be measured before and after each sample.

- DNPH carbonyl sampling: Although DNPH-coated silica Sep-Pak cartridges can be obtained commercially (Waters Associates, Milford, NH), the Sep-Pak C₁₈ cartridges are in most widespread use. Arnts and Tejada (1989) report negative interferences from ozone on formaldehyde for the silica-gel substrates. Even though EPA TO-11A recommends the silica-gel cartridge preceded by a potassium iodide (KI) scrubber to remove ozone, the reliability of this method is unproven (Zielinska and Fujita, 1996) and it may also remove some of the higher carbon number (>C₄) carbonyls (Fung, 1998).
- For solvent extractable particulate organics, carbon, and ion analyses, the Whatman QMA filter is used for sampling. Blank filter levels need to be verified, as they may be excessive in this type of filter. The Pallflex ultrapure QAT-UP filter was developed for carbon speciation, whereas the QMA filter contains a borosilicate glass binder for PM₁₀ compliance sampling that decreases its friability, but increases its blank levels.

3.2 Sampling Frequency

The program plan specifies samples taken every sixth day for PM_{2.5}, carbonyls, and VOCs, every 12th day for hexavalent chromium, and twice per month for PAHs, PCCDs, PCDFs, and PCBs. VOCs and carbonyls are acquired only at the TW and CW sites. PM_{2.5} samples are taken at the TW, HT, and NMK sites, and the PAH, PCBs, PCDDs, and PCDFs are measured at the four sites for a year from November 5, 2000 through October 27, 2001. The EPD sampling schedules showed that sampling dates differ for the particulate and gaseous samples. Maximum benefit will be gained by having as many measurements as possible available on the same days. The 12-day and twice per month schedules should coincide with every other sampling day in the sixth day schedule. PM_{2.5} samples are taken on three consecutive days, beginning on the first day of the sixth day schedule. Collocated R&P samplers take parallel quartz filters on the first day, parallel Teflon and quartz filters on the second day, and parallel quartz filters on the third day. The purpose of this is to acquire many quartz filters that can be submitted to solvent-extractable organics analysis, as a single filter does not have sufficient material to yield many compound concentrations above the GC/MS detection limits

Sampling dates should be selected from the U.S. EPA sixth day sampling schedule. The first sample for 2001 is 1/1, with subsequent samples on 1/7, 1/13, 1/19, 1/26 etc. throughout the year. Less frequent sampling should skip one or more samples between these dates (e.g., 1/1, 1/13, 1/26) while more frequent sampling should add samples at regular intervals between these dates (e.g., 1/1, 1/4, 1/7, 1/10, etc.). This schedule was formulated by the U.S. EPA in the 1970s to provide a sampling frequency of approximately once per week without sampling on the same day with each sample. The parallel PM_{2.5} Teflon and quartz filters should be taken on the first day and analyzed for mass, elements, ions, and carbon. The extractable organic samples can be taken on the following days, but these will only be useful as quarterly averages when compared with the averages from the PM_{2.5} samples taken the day before. It would be better to use an additional PUF sampler (preferably with a PM_{2.5} inlet, although this isn't essential because most

of these organic materials are in the PM_{2.5} fraction) alongside the PM_{2.5} samplers for this purpose. Since the toxic organic compounds are acquired every 12th day, the solvent extractable organics could be acquired with the same samplers on the intervening sixth day.

4. FILTER WEIGHING

Gravimetric analysis of the 47 mm diameter Teflon-membrane and quartz-fiber filters used in the Partisol samplers are performed in a temperature ($21.5 \pm 1.5^\circ\text{C}$) and relative humidity ($35 \pm 5\%$) controlled environmental clean room at the EPD. Intake air is passed through a HEPA filter to remove outdoor particles and positive pressure is maintained. The Mettler MT5 microbalance is located on a heavy marble slab inside a glove box. Unexposed and exposed filters are conditioned for 24-hours prior to weighing.

Although the current filter weighing procedures are adequate, their efficiency and accuracy can be improved with the following modifications:

- Electrostatic charge can be more efficiently neutralized. Current procedures manually locate each filter over a single ²¹⁰Po antistatic strip (Staticmaster ionizing unit, Model 24500, Grand Island, NY) prior to weighing. The filter can be placed inside an antistatic box that completely surrounds the filter, as shown in Figure 1. This reduces the charge more rapidly and frees the balance operator to weigh the prior filter. ²¹⁰Po has a 138 half life and these should be replaced every six to nine months. The change date can be posted on the glove box so that strips can be re-ordered. These need to be ordered new; they will decay if they are stockpiled.
- National Institute of Science and Technology (NIST) Class 1.1 (formerly Class M) traceable weights of 200.000 mg with accuracy of $\pm 5 \mu\text{g}$ are recommended for balance calibration and performance testing.
- Filters and standard weights should be handled with separate flat-tipped, non-serrated, stainless steel forceps (Millipore No. 62-00006, San Francisco, CA) to prevent contamination.
- Replicate weights should be performed by a separate operator, preferably on a different day, to evaluate reproducibility and assure that differences do not exceed reasonable tolerances ($\pm 10 \mu\text{g}$).
- Establish ID system that uses bar code labels. These can be rapidly and accurately scanned from filter containers and data sheets with a bar code reader (e.g., No. MH 941K barcode scanner, Metrologic Instruments, Inc., Blackwood, NJ) interfaced to the data acquisition computer. An eight-character code that contains alphanumeric characters for the project, sampling site, filter type, and a sequential number is most useful for tracking sample chain of custody.
- Use lint-free bench paper, disposable sheets of absorbent paper with a polyethylene backing (e.g. Fisher Bench Protectors, Catalogue # 12-0079-186).

- Rinse filter holders and support grids with tap water, followed by two rinses in distilled-deionized water (DDW), with air dry. This should follow the unloading of each exposed filter from field sampling. The dust-free spray currently used may not provide sufficient cleaning for dirty holders.
- Minimize vacuuming and use of solvents, such as ammonia, in the clean room. A damp mop with clean water is sufficient to remove dirt. Install a CleanWalk (3M, Catalogue No. 5801, St. Paul, MN) floor mat at the entrance to the clean room to remove deposits from shoes.

5. ANALYTICAL METHODS

Standard Operating Procedures (SOPs) need to be established and documented for all of the actions carried out in this study. Table 1 specifies the elements that need to be included in these procedures, as is being done for the U.S. EPA's Supersite Program. The EPA compendium procedures for organic analysis (TO) are thorough and provide a good starting point for canister, DNPH, and Filter/PUF sampling and analysis. These procedures limit the number of organic compounds quantified, and the recommendations should be considered a minimum. As noted in the procedures, many more compounds can and should be quantified from the analyses to characterize PM_{2.5}. The procedures do not follow a standard format, and many of the steps are instrument-specific and need to be adapted to the specific hardware and software available in the EPD laboratories.

There are many useful parts of some TO procedures that should be incorporated into all of them. For example, Method TO-13 for PAH analysis provides a detailed five-level standard for calibration in the range of 0.1 to 2.5 ng/μl. Method TO-9A for PCDDs and PCDFs and Method TO-11A for carbonyls provide for only stock or spiking solutions without specifying level and concentration ranges. Methods TO-4 (PCBs) and TO-14A (VOCs) are even less explicit on calibration. The laboratory should provide a list of the species to be quantified within each laboratory with corresponding instrumental minimum detection limits (MDLs), sample lower quantifiable limits (LQLs), and calibration compounds and levels that span the range of concentrations to be analyzed.

6. QUALITY CONTROL AND QUALITY ASSURANCE

Field and laboratory inspections show that field sampling and gravimetric analyses are being performed with great care. Written procedures are still necessary, however, to document the actions taken and to provide instructions for future staff that might not be as experienced as the current staff. Comparisons of analytical results with another laboratory should be conducted on ~20 sample sets.

The program plan indicates quarterly collocated sampling and analysis, but a schedule for this sampling needs to be established and followed. Prior to field sampling, acceptance tests should be performed on ~2% of the substrates to assure that these are free of contamination. Acceptance testing applies the same analyses to these filters that will be applied to the sampled filters. This is especially important for VOC canisters after they have been cleaned. It is also a good idea to fill these samples with a standard of known composition and to analyze them after a

few days of storage to evaluate sample deposition to the walls of the canister. Samples should be sealed in air-tight containers and stored under refrigeration before and after sampling.

Future studies should create and follow a Quality Assurance Project Plan (QAPP) that specifies quality assurance and quality control activities. Annual or semi-annual systems and performance audits as well as interlaboratory comparisons need to be an integral part of Hong Kong EPD monitoring efforts.

Related DRI Standard Operating Procedures (SOPs) for gravimetric analysis, sample shipping and receiving, chain of custody, and filter pack assembly have been provided to EPD as guidance for creating project-specific procedures.

7. REFERENCES

Arnts, R.R. and Tejada, S.B. (1989) 2,4-Dinitrophenylhydrazine-coated silica gel cartridge method for determination of formaldehyde in air: Identification of an ozone interference. *Environ. Sci. Technol.* **23**, 1428-1430.

Fung, K.K. (1998) Comparison of carbonyl sampling using C18 and silica DNPH cartridges. *Annual Meeting of the American Geophysical Union*, San Francisco, CA.

Zielinska, B. and Fujita, E.M. (1994) Organic gas sampling. In *Environmental Sampling for Trace Analysis*, Markert, B., Ed. VCH Publishers, New York, NY, pp. 163-184.

Table 1. Elements of a Standard Operating Procedure

1.0 General Information

- 1.1 Scope and Applicability
- 1.2 Summary of Method
- 1.3 Definitions
- 1.4 Health and Safety Warnings (indicating operations that could result in personal injury or loss of life and explaining what will happen if the procedure is not followed or is followed incorrectly; listed here and at the critical steps in the procedure)
- 1.5 Cautions (indicating activities that could result in equipment damage, degradation of sample, or possible invalidation of results; listed here and at the critical steps in the procedure)
- 1.6 Interferences
- 1.7 Personnel Qualifications

2.0 Installation/Collection Procedures

- 2.1 Apparatus and Materials (physical description, initial start-up)
- 2.2 Instrument or Method Calibration (apparatus, standards, as-is calibration, final calibration)
- 2.3 Sample Collection
- 2.4 Handling and Preservation
- 2.5 Sample Preparation and Analysis
- 2.6 Troubleshooting

3.0 Quality Control and Quality Assurance

- 3.1 Routine Service Checks
 - 3.1.1 General Information
 - 3.1.2 Frequency of QC Checks (e.g., daily, weekly, monthly, annually)
- 3.2 Detailed Maintenance Procedures
- 3.3 Acceptance Testing Procedures
 - 3.3.1 General Information
 - 3.3.2 Physical Inspection
 - 3.3.3 Operational Tests
 - 3.3.4 Final Review
- 3.4 Quality Assurance
 - 3.4.1 Performance Audit Schedule
 - 3.4.2 Systems Audit Schedule
 - 3.4.3 Data Validation Procedure Summary
- 3.4 Quality Assurance
 - 3.4.1 Performance Audit Schedule
 - 3.4.2 Systems Audit Schedule
 - 3.4.3 Data Validation Procedure Summary
- 3.5 Checklist

4.0 References

Figure 1. Example of anti-static box for neutralizing charges on filters prior to weighing.

