QUALITY ASSURANCE PROJECT PLAN (QAPjP) and QA Report for Pacific 2001

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1. **Principal Investigator**
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2. **Team Members**
   Wenzie Ng

3. **Measurement Program**
   Tropospheric gas-phase formaldehyde measurements

4. **Measurement Species and Units**
   Gas-phase HCHO …… ppbv

5. **Representative Size Range (if PM)**
   NA

6. **Measurement Platform (surface, airborne)**
   HCHO: Surface - 3 m above ground level (Langley)
   Surface - 8 m above ground level (Sumas Mountain)

7. **Measurement Sites (surface only)**
   HCHO: Langley, Sumas Mountain

8. **Measurement Objective(s)**
   To provide continuous measurements of formaldehyde at suburban and elevated locations.

9. **Measurement Details**
   9.1. Field Measurements
   9.1.1. Measurement Principle
   HCHO: Coil stripper, Hantzsch reaction, and fluorescence detection
   9.1.2. Instrumentation (Manufacturer/Model)
   HCHO:
   There are two instruments based on the same chemistry. Formaldehyde is stripped from the air into a H_2SO_4 aqueous solution through a glass coil. The dissolved HCHO is then reacted with the ketone (2,4-pentanedione) in an aqueous solution of ammonium acetate and acetic acid. Formation of the reaction product, 3,5-diacetyl 1,4-dihydrolutidine (DDL), takes place in a heated reaction coil. The DDL is quantified through fluorescence.
   Langley: the instrument was built in-house, liquid flow rate is 0.8 mL/min, air flow rate is 2 L/min

   Sumas Mountain: the instrument was manufactured by Aerolaser (Model 4021), liquid flow rate 0.45 L/min, air flow rate 1 L/min

9.1.3. Flow System

9.1.4. Inlet Height Above Ground (if surface)
HCHO Langley – 3 m above ground
HCHO Sumas Mountain – 8 m above ground

9.1.5. Nominal Flow Rate
HCHO Langley: air flow 2 L/min
HCHO Sumas Mountain: air flow 1 L/min

9.1.6. Flow Measurement/Control
Langley: Mass flow controller
Sumas Mountain: Mass flow controller

9.1.7. Flow Temperature and Pressure
STP: 0C and 1 atm

9.1.8. Sampling Times/Period/Frequency
1-second values averaged to 1 minute

9.1.9. Sampling Methods
NA

9.1.10. Filter Type/Coating Type/Reagent Type
NA

9.1.11. Planned Changes to Instruments or Methods During Study
N/A

9.2. Laboratory Measurements (If Applicable)

9.2.1. Laboratory Name and Address
N/A

9.2.2. Analytical Method(s)
N/A

9.2.3. Sample Extraction or Work-up
N/A

9.2.4. Analytical Detection Limits
N/A

10. Quality Assurance/Quality Control

10.1. Field Quality Assurance/Quality Control

10.1.1. Traceability
Air flow rates are referenced to an MSC MKS primary flow standard.

Formaldehyde stock solution is standardized by iodometric tiration. The concentration of the sodium thiosulphate used in the titration is NIST traceable.

10.1.2. Calibration

Instruments will be calibrated both with liquid solutions and gas permeation systems.

Langley : The in-house instrument will be calibrated daily with liquid standards and weekly through the inlet with a gas-phase standard supplied by a permeation system.

Sumas Mountain: Aerolaser instrument will be calibrated daily with liquid standards and weekly through the inlet with a gas-phase standard supplied by a permeation system.

10.1.3. Zeros and spans

Zeros will be done hourly for both instruments.
Spans will be done every six hours on the Aerolaser instrument with an internal permeation source.

10.1.4. Blanks

N/A

10.1.5. Field Quality Control procedures

All solutions will be prepared in the Animal Health Centre (MAFF) laboratory under controlled conditions. Both the stripping and reagent solutions will sit in coolers at the site. This preserves the reagent and also increases the stripping efficiency. Reagent and stripping bottles are glass and have stoppers with vent traps to prevent contamination of the solutions by ambient air.
The liquid flow rates will be checked regularly. Gloves will be worn when changing solutions. Peristaltic tubing will be inspected daily and changed twice during the study.
Each instrument has a dedicated inlet line (1/4” Teflon) with an inlet filter (5 um, Millipore Teflon) that will be changed daily.

10.1.6. Precision determination

Two instruments will be run in the lab side by side prior to the study. Instrument response to repeated calibration points supplied by a permeation-dilution system will be examined.

10.1.7. Comparison with other measurements

Langley: The in-house HCHO can be compared to the 3-hour averaged HCHO values from the DNPH cartridges (Wang, EPS).

Sumas Mountain: The Aerolaser HCHO can be compared to the 2-hourly HCHO values reported through the DNPH-coated fused silica cartridges, HPLC method (McLaren, York U).
Comparability with other methods including the TDLAS and the cartridges has been described in Macdonald et al., 1999.

10.1.8. Inspections and Audits

10.2. Laboratory Quality Assurance/Quality Control

10.2.1. Traceability

N/A

10.2.2. Calibration procedures

N/A

10.2.3. Blanks

N/A

10.2.4. Other lab QC

N/A

10.2.5. Precision determination

N/A

10.2.6. Comparison with other methods

N/A

10.2.7. Audits

N/A

11. Data Management and Quality Control

11.1. Raw Data Recording

Langley HCHO in-house instrument: data will be recorded through Labview on a PC at 1-second intervals and logged as 1-minute averages.

Sumas Mountain HCHO Aerolaser instrument: instrument is controlled and data logged through instrument-specific software, digital output. An analog output of the raw signal voltage is also available and this will be connected to Labview, logged every second and saved as 1-minute averages.

11.2. Final Data Reporting

Both instruments – Data will be reported as 1-minute and 10-minute data.

11.3. Data Quality Control and Validation

All reported data values will be flagged as either Valid (V) or Invalid (I).

All raw data will be inspected and zeros, calibrations, spans, power failures, inlet filter changes, flow calibraton periods will be flagged as invalid.

11.4. Validity Flags

V0 Valid Value
V1 Valid value but comprised wholly or partially of below-MDL data
M1 Missing value because no value is available
I1 Invalid – power failure
I2 Invalid – zero
I3 Invalid – calibration point 1
I4 Invalid - calibration point 2
I5 Invalid – flow measurements or instrument testing
I6 Invalid – other instrument error

11.5. Below Method Detection Limit Values

Detection limit: 100 pptv (3 times the standard deviation of the zero-point noise)

11.6. Derived Parameters

The fluorescence signal proportional to the HCHO is the difference between the measured value and a zero baseline. The signal is somewhat temperature dependent thus zeros need to be done hourly to establish a zero baseline.

11.7. Explanation of Zero or Negative Data

12. Data Quality Objectives (Pre-Study)

12.1. Accuracy

Accuracy objective is ±10% at 1 ppbv. This is determined by the difference between the instrument calibrated readings and those produced by a laboratory permeation-dilution source before and after the study.

12.2. Precision

Precision objective is ±5% at 1 ppbv determined from the instrument response on multiple days to the given mixing ratio produced by a portable permeation-dilution system.

12.3. Comparability

Continuous HCHO at Langley can be averaged up to the period of sampling for the DNPH cartridges. Previous comparisons for 4-hour samples showed agreement to within 20% (Macdonald et al., 2001). Comparison between the Hantzsch continuous method and the TDL was within ±3% (Macdonald et al., 1999).

Previous comparisons have not been made between the Hantzsch method and the DNPH-HPLC method expected at Sumas (McLaren).

12.4. Representativeness

- The measurements at the Langley site will be representative of processed air pollution in which secondary pollutants, such as ozone, and secondary particulate matter will have formed.
- The measurements at the Sumas Mountain site will be representative of processed air pollution with significant influence from biogenic and ammonia sources. They will also be representative of the free boundary layer air and thus representative of the processes affecting the evolution of pollutants throughout the diurnal cycle. They will also capture the visibility reduction at the eastern end of the Lower Fraser valley.

12.5. Completeness

Formaldehyde completeness objective = 85%
This is based on one-minute data, 10 % of which is invalid because of zeros and calibrations. The additional 5% loss is expected because of power failures or instrument failure.

12.6. Other Quality Information

Data at Sumas may be impacted by infrequent vehicular traffic at the site. These periods will be flagged and removed.

End of Pre-Study QAPjP

Start of Post-Study QA Report

13. Significant Changes to Site, Instruments or Methods During Study

14. Post-study Data Quality Indicators (DQIs)

14.1.1. Accuracy

14.1.2. Precision

14.1.3. Comparability

14.1.4. Representativeness

14.1.5. Completeness

14.2. Blank correction (describe whether done and method used):

14.3. Other Quality Information

15. References:

Macdonald. A.M. H.A. Wiebe, S.M. Li, H. Dryfhout-Clark, K. Asalian, G. Lu, D. Wang, C.L. Schiller, G.W. Harris, A.L. Sumner, P.B. Shepson, “Results of a formaldehyde intercomparison study in Ontario”, Report ACSD-99-001, Environment Canada, 1999.

A. M. Macdonald, P. A. Makar, K. G. Anlauf, K.L. Hayden, J.W. Bottenheim, D. Wang and T. Dann, Summertime Formaldehyde at a High Elevation Site in Quebec, JGR 2001 in press.