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

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2. **Team Members**
   John Liggio (graduate student)
   Mauro Aiello (graduate student)

3. **Measurement Program**
   Automated HPLC measurements of gaseous organic carbonyls

4. **Measurement Species and Units**
   Gas, Aldehydes and ketones ppbv

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

6. **Measurement Platform (surface, airborne)**
   Teflon Line – 5 m above ground level.

7. **Measurement Sites (surface only)**
   Sumas Mountain

8. **Measurement Objective(s)**
9. **Measurement Details**
   9.1. Field Measurements
      9.1.1. Measurement Principle
      Automated carbonyl sampling and measurement instrument including the following components/steps: gaseous sampling system, custom stainless steel silica cartridge coated with acidified DNPH, micro-HPLC system for online injection and analysis of sample, UV detection with custom micro-flow cell, deuterium lamp, fiber optic spectrometer with CCD detection.
      9.1.2. Instrumentation (Manufacturer/Model)
      Micro-Tech HPLC, 1mm x 25cm C18, 3um, column, H2O/ACN gradient, Oriel Deuterium lamp with fiber optic delivery of light to custom flow cell, fiber optic collection of light to Ocean Optics S2000 fiber optic spectrometer. Custom valving performs the following functions, loading acidified DNPH solution (under UHP He pressure) onto cartridge, UHP He flushing of cartridge, sampling of air through cartridge, fill cartridge with water, inject cartridge contents into HPLC, clean cartridge with ACN. All instrumention functions and data storage by PC computer.

9.1.3. Flow System

Flow through on site manifold will be sampled through short length teflon tubing at ca. 50 mL/min regulated by Tylon Mass flow controller. The following components are in the sampling stream: 1) 2 um frit (to eliminate particles), small cartridge packed with KI (to remove ozone), DNPH cartridge (to trap carbonyls), valve, MFC, pump.

9.1.4. Inlet Height Above Ground (if surface)

~ 3-5 m above trailer top.

9.1.5. Nominal Flow Rate

50 mL/min sampled from a 4" manifold operating at ca. 3.0 m3/min.

9.1.6. Flow Measurement/Control

mass flow controller

9.1.7. Flow Temperature and Pressure

25 degrees C and 1 atmosphere

9.1.8. Sampling Times/Period/Frequency

3 hour cycle. 7 measurements per day + 1 blank.

9.1.9. Sampling Methods

sample is analyzed on site by automated instrument.

9.1.10. Filter Type/Coating Type/Reagent Type

0.001M 2,4-nitrophenylhydrazine, pH =3.0, silica cartridge.

9.1.11. Planned Changes to Instruments or Methods During Study

9.2. Laboratory Measurements (If Applicable)

9.2.1. Laboratory Name and Address

Robert McLaren's laboratory, Dept of Chemistry, York University.

9.2.2. Analytical Method(s)

9.2.3. Sample Extraction or Work-up

9.2.4. Analytical Detection Limits

~50 – 100ppt detection limits for a range of carbonyls including formaldehyde, acetaldehyde, acetone, propanal, glyoxal, methylglyoxal, m,p-tolualdehyde, benzaldehyde

10. Quality Assurance/Quality Control

10.1. Field Quality Assurance/Quality Control

10.1.1. Traceability

Mass flow controller calibrated with a gas clock in house. Calibrations for carbonyls are traced to primary standards of solid carbonyl hydrazones synthesized and purified in our labs.

10.1.2. Calibration

Gravimetric standards of hydrazones are serially diluted in acetonitrile for calibration, before and after study. Collection and reaction efficiency of cartridge for carbonyls has been measured under operating conditions to be 100% +/- 7%.

10.1.3. Zeros and spans

10.1.4. Blanks

1 blank per day will be evaluated, static DNPH load without air sampling. Although zero air could be sampled for a blank, this requires extreme cleanup of the air using liquid Argon, and will not be performed under field conditions.

10.1.5. Field Quality Control procedures

Custom QC procedures for the instrument. H2O and DNPH solution are protected by UHP He to virtually eliminate blank signals and drift.

10.1.6. Precision determination

Precision is being determined before field study and after by sampling standard dynamically generated gas samples. Precision, including effects of mass flow control is +/- 3% for acetone.

10.1.7. Comparison with other measurements

Hopefully a comparison can be made for HCHO using measurements performed by another PI at same site (A.M MacDonald)

10.1.8. Inspections and Audits

10.2. Laboratory Quality Assurance/Quality Control

10.2.1. Traceability

10.2.2. Calibration procedures

10.2.3. Blanks

10.2.4. Other lab QC

10.2.5. Precision determination

10.2.6. Comparison with other methods

10.2.7. Audits

11. Data Management and Quality Control

11.1. Raw Data Recording

flow control is monitored manuallly by data notebook throughout study. Precision is +/- 2% over long periods of time (several days). All other data will be stored electronically, especially the individual chromatograms.

11.2. Final Data Reporting

90 minute average during integrated sampling period, one period every 3 hours.

11.3. Data Quality Control and Validation

All reported data will be flagged as valid or invalid. Flows will be checked, all instrumental parameters must be functioning normally, data will be blank corrected if necessary using blank determined that day, species will be identified by retention time and UV spectra, spectral purity will be inspected for each peak, possible chromatographic overlaps will be flagged.

11.4. Validity Flags

VO, V1

11.5. Below Method Detection Limit Values

MDL will be identified using standard analytical definition, 3 sigma of blank/slope. Standard deviation of blank is determined by integrating appropriate sections of chromatogram baseline for blank samples multiple times an for multiple samples. Values below detection limits will be reported as less than the detection limit, e.g., < 50 ppt.

11.6. Derived Parameters

11.7. Explanation of Zero or Negative Data

12. Data Quality Objectives (Pre-Study)

12.1. Accuracy

The accuracy objective is +/- 20% for each individual carbonyl species when it is above the limit of quantification (3.3 x detection limit.)

12.2. Precision

The precision objective is +/- 5% for each individual carbonyl species when it is above the limit of quantification. This will be determined in advance using dynamic gas standards.

12.3. Comparability

12.4. Representativeness

Depending on conditions, the measurements at this Sumas site can be representative of processed urban air masses with influence from primary an secondary biogenic sources. The measurements can also be representative of direct biogenic emissions. Daytime measurements will likely be representive of the boundary layer, while nightime measurements will likely be decoupled from the surface inversion due to the elevation of this site (300m asl).

12.5. Completeness

Carbonyl completeness objective = 80%, where 100% = 7 valid samples per day (~ 8-12 species above detection limit).

12.6. Other Quality Information

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: