

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

**Prepared by: Jacek Stupak**

**Date: June 22, 2001**

## Table of Contents

1.	Principal Investigator .....	3
2.	Team Members .....	3
3.	Measurement Program.....	3
4.	Measurement Species and Units .....	3
5.	Representative Size Range (if PM) .....	3
6.	Measurement Platform (surface, airborne).....	3
7.	Measurement Sites (surface only).....	3
8.	Measurement Objective(s) .....	3
9.	Measurement Details.....	3
9.1.	Field Measurements .....	3
9.1.1.	Measurement Principle .....	3
9.1.2.	Instrumentation (Manufacturer/Model).....	3
9.1.3.	Flow System .....	3
9.1.4.	Inlet Height Above Ground (if surface) .....	3
9.1.5.	Nominal Flow Rate.....	3
9.1.6.	Flow Measurement/Control.....	3
9.1.7.	Flow Temperature and Pressure .....	4
9.1.8.	Sampling Times/Period/Frequency.....	4
9.1.9.	Sampling Methods .....	4
9.1.10.	Filter Type/Coating Type/Reagent Type.....	4
9.1.11.	Planned Changes to Instruments or Methods During Study .....	4
9.2.	Laboratory Measurements (If Applicable) .....	4
9.2.1.	Laboratory Name and Address .....	4
9.2.2.	Analytical Method(s) .....	4
9.2.3.	Sample Extraction or Work-up.....	5
9.2.4.	Analytical Detection Limits.....	5
	Instrumental detection limits were approximated from the signal to noise ratios .....	5
10.	Quality Assurance/Quality Control .....	6
10.1.	Field Quality Assurance/Quality Control .....	6
10.1.1.	Traceability.....	6
10.1.2.	Calibration .....	6
	Flow recorder is calibrated using a Kruz Model 330C Type U.O. Adjustable orifice calibrator. ....	6
10.1.3.	Zeros and spans .....	6
10.1.4.	Blanks .....	6
	~10% of filters will be reserved for highvol loaded blank as per SOP.....	6
10.1.5.	Field Quality Control procedures .....	6
10.1.6.	Precision determination .....	6
10.1.7.	Comparison with other measurements .....	6
10.1.8.	Inspections and Audits.....	6
10.2.	Laboratory Quality Assurance/Quality Control.....	6
10.2.1.	Traceability.....	6
10.2.2.	Calibration procedures.....	6
10.2.3.	Blanks .....	7
10.2.4.	Precision determination .....	7
10.2.5.	Comparison with other methods .....	7
10.2.6.	Audits .....	7
11.	Data Management and Quality Control .....	7

## QAPjP / QA Report

11.1.	Raw Data Recording.....	7
11.2.	Final Data Reporting.....	7
11.3.	Data Quality Control and Validation.....	7
11.4.	Validity Flags.....	7
11.5.	Below Method Detection Limit Values .....	8
11.6.	Derived Parameters .....	8
11.7.	Explanation of Zero or Negative Data.....	8
12.	Data Quality Objectives (Pre-Study) .....	8
12.1.	Accuracy .....	8
12.2.	Precision .....	8
12.3.	Comparability .....	8
12.4.	Representativeness .....	8
12.5.	Completeness .....	9
12.6.	Other Quality Information.....	9
13.	Significant Changes to Site, Instruments or Methods During Study .....	10
14.	Post-study Data Quality Indicators (DQIs) .....	10
14.1.1.	Accuracy .....	10
14.1.2.	Precision .....	10
14.1.3.	Comparability .....	10
14.1.4.	Representativeness .....	10
14.1.5.	Completeness .....	10
14.2.	Blank correction (describe whether done and method used): .....	10
14.3.	Other Quality Information.....	10
15.	References: .....	10

**1. Principal Investigator**

Jochen Rudolph, York University, 4700 Keele St., Toronto, ON, M3J 1P6

**2. Team Members**

Jacek Stupak, Shidong Gao

**3. Measurement Program**

Hivol measurements of aromatic organic acids and nitro-phenols.

**4. Measurement Species and Units**

Aromatic organic acids: ng/m<sup>3</sup> at 25°C and 1atm.

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

Hivol: < 2.5 µm

**6. Measurement Platform (surface, airborne)**

Hivol: Surface 1.6 m above ground level

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

Slocan Park, Langley, Sumas Mountain, Cassiar Tunnel

**8. Measurement Objective(s)**

**9. Measurement Details**

**9.1. Field Measurements**

**9.1.1. Measurement Principle**

Filter collection using a Hi-volume sampler

**9.1.2. Instrumentation (Manufacturer/Model)**

Hivol sampler: General Metal Works Model 2000H

**9.1.3. Flow System**

Hivol system: The flow of the hivol is nominally 40 cfm and changes (somewhat) as the filter loading increases. The motor outlet is connected to a 20 feet hose that exhausts downwind of the sampler. For some York measurements, PM 2.5µm cutoff will be provided with a conventional PM10 impactor head converted with a Tisch Environmental PM2.5 conversion kit (TE-6001-2.5)

**9.1.4. Inlet Height Above Ground (if surface)**

Hivol: 2 m above ground level on top of platform.

**9.1.5. Nominal Flow Rate**

1.13 m<sup>3</sup>/min (40 ft<sup>3</sup>/min)

**9.1.6. Flow Measurement/Control**

Flow rate is recorded on a Dickson Model 3-B-L Circular chart recorder , Chart no 106.

**9.1.7. Flow Temperature and Pressure**

N/A

**9.1.8. Sampling Times/Period/Frequency**

2 -12 hour samples per day

**9.1.9. Sampling Methods**

The SOP will be very similar to those written up by Pierrette Blanchard for quartz fiber filters. Briefly, quartz coated filters will be pre-cleaned by firing at either 550C (SP, L) or 750C (Sumas). Samples will be stored in custom designed metal storage containers for the study. After sampling, samples will be stored individually in tin foil with numerical codes identifying the filters, again placed in the predesigned boxes and frozen in central freezers

Samples will be weighed, cut into 8 parts and stored in glass jars filled with nitrogen gas.

**9.1.10. Filter Type/Coating Type/Reagent Type**

Pall-Gellman Tissuquartz filters (part # 7204) ,8 x 10 in.

**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**

Prof. Rudolph/Prof. McLaren Chemistry laboratory, Petrie 335, York University.

**9.2.2. Analytical Method(s)**

Capillary electrophoresis: Hewlett-Packard 3D-CE(Walbronn, Germany) equipped with a diode array detector and buffer replenishment system; 75 um inner diameter, 200um detector path length capillaries will be used for the measurements.

Measured Species:

4-NO <sub>2</sub> -phenol	capillary electrophoresis-DAD
benzoic acid	capillary electrophoresis-DAD
2-OH-benzoic acid	capillary electrophoresis-DAD
3-OH-benzoic acid	capillary electrophoresis-DAD
4-OH-benzoic acid	capillary electrophoresis-DAD
4-me-phthalic acid	capillary electrophoresis-DAD
p-phthalic acid	capillary electrophoresis-DAD
m-phthalic acid	capillary electrophoresis-DAD
o-phthalic acid	capillary electrophoresis-DAD
1,2,3-bz(COOH) <sub>3</sub>	capillary electrophoresis-DAD

1,2,4-bz(COOH) <sub>3</sub>	capillary electrophoresis-DAD
1,2,4,5-bz(COOH) <sub>4</sub>	capillary electrophoresis-DAD

### 9.2.3. Sample Extraction or Work-up

Filters extracted: with 1ml 0.1M HCl and 10ml diethyl ether by mechanical stirring; nitrogen blow-down of the separated organic layer; residue dissolved in 100ul 2mM pH 9.9 borate and analysed by capillary electrophoresis.

### 9.2.4. Analytical Detection Limits

Instrumental detection limits were approximated from the signal to noise ratios of standard peaks: three times the standard deviation of integrated baseline noise divided by the peak area over amount. Detection limits in solution are given.

Substance (wavelength used for calibration)	Instrumental Detection Limit (ng)
4-nitro-phenol (405nm)	7.6
benzoate (192 nm)	4.1
2-OH-benzoate (201 nm; peak height)	4.1
3-OH-benzoate (201 nm)	4.8
4-OH-benzoate (280 nm)	9.1
4-me-phthalate (199 nm)	4.9
p-phthalate (239 nm)	11.5
m-phthalate (206 nm)	4.2
o-phthalate (195 nm)	5.5
1,2,3-bz(COOH) <sub>3</sub> (200nm)	8.8
1,2,4-bz(COOH) <sub>3</sub> (201nm)	6.4
1,3,5-bz(COOH) <sub>3</sub> (207 nm)	12.8

For method detection limits, the standard deviation of averaged blank values was multiplied by three and divided by the calibration slope; this value was then divided by 1500 m<sup>3</sup> - the average air volume for a 24 hour sampling time. For peaks not detected in blanks the instrumental detection limit divided by the average sampling volume is given. Blanks values used are those obtained during Sontas 2000 in Hamilton.

Substance (wavelength used for calibration)	Method Detection Limit (pg/m <sup>3</sup> )
4-nitro-phenol (405nm)	5.1
benzoate (192 nm)	160.8
2-OH-benzoate (201 nm; peak height)	27.4
3-OH-benzoate (201 nm)	3.2
4-OH-benzoate (280 nm)	6.1
4-me-phthalate (199 nm)	3.3
p-phthalate (239 nm)	7.7
m-phthalate (206 nm)	2.8
o-phthalate (195 nm)	44.8

1,2,3-bz(COOH) <sub>3</sub> (200nm)	5.9
1,2,4-bz(COOH) <sub>3</sub> (201nm)	4.3
1,2,4,5-bz(COOH) <sub>3</sub> (207 nm)	8.5

## 10. Quality Assurance/Quality Control

### 10.1. Field Quality Assurance/Quality Control

#### 10.1.1. Traceability

Flow rate measurements and adjustments will be made on a weekly basis or as needed.

#### 10.1.2. Calibration

Flow recorder is calibrated using a Kruz Model 330C Type U.O. Adjustable orifice calibrator.

#### 10.1.3. Zeros and spans

N/A

#### 10.1.4. Blanks

~10% of filters will be reserved for highvol loaded blank as per SOP.

#### 10.1.5. Field Quality Control procedures

Disposable gloves will be worn when loading/unloading filters; filters will be loaded/unloaded in a clean room; filters will be inspected for holes when loaded and unloaded in the lab and field;

#### 10.1.6. Precision determination

N/A

#### 10.1.7. Comparison with other measurements

N/A

#### 10.1.8. Inspections and Audits

N/A

### 10.2. Laboratory Quality Assurance/Quality Control

#### 10.2.1. Traceability

All standards were obtained from Sigma Aldrich, except p-phthalic acid, which was obtained from Chem Service(West Chester, PA).

#### 10.2.2. Calibration procedures

An internal standard calibration will be used for quantitation. Calibration standards will be prepared by dilution of gravimetrically prepared stock solution using standard chemicals indicated above. The calibration data will be used to quantify the data set.

**10.2.3. Blanks**

Filter blanks, buffer blanks, extraction blanks

Other lab QC

Recovery tests with the extraction method described above gave the results shown below. For 1,2,3-bz(COOH)<sub>3</sub> and 1,2,4,5-bz(COOH)<sub>4</sub>, measurements should be treated as lower limits.

	#1	#2	#3	#4	#5	Avg. Rec. %	RSD
m-toluate	102.9	89.2	97.7	96.8	99.8	97.3	5.2
4-NO <sub>2</sub> -phenol	89.5	93.4	91.5	90.6	90.6	91.1	1.6
benzoate	96.5	101.1	107.7	101.6	101.4	101.7	3.9
2-OH-benzoate	93.6	96.4	108.4	99.0	102.4	100.0	5.7
3-OH-benzoate	98.2	101.0	91.4	100.8	101.0	98.5	4.2
4-OH-benzoate	89.9	96.2	104.5	96.7	97.0	96.9	5.3
4-Me-phthalate	82.6	82.0	97.8	108.3	105.5	95.2	13.0
p-phthalate	82.4	77.3	93.9	106.4	106.4	93.3	14.4
m-phthalate	85.6	85.3	100.1	109.3	109.7	98.0	12.3
o-phthalate	83.5	80.4	98.5	109.3	103.2	95.0	13.2
1,2,3-bz(COOH) <sub>3</sub>	51.0	55.5	62.8	66.2	61.1	59.3	10.2
1,2,4-bz(COOH) <sub>3</sub>	93.6	93.3	116.5	96.6	96.5	99.3	9.8
1,3,5-bz(COOH) <sub>3</sub>	77.4	80.4	90.2	111.6	98.0	91.5	15.2
1,2,4,5-bz(COOH) <sub>4</sub>	50.1	59.5	65.1	69.1	63.1	61.4	11.7

**10.2.4. Precision determination**

N/A

**10.2.5. Comparison with other methods**

N/A

**10.2.6. Audits**

N/A

**11. Data Management and Quality Control****11.1. Raw Data Recording**

Flow on high vol to be recorded as per SOP.

**11.2. Final Data Reporting**

12 hour integrated sample.

**11.3. Data Quality Control and Validation**

All reported data will be flagged as valid or invalid. Flows will be checked as to whether they are within +/- 10% of nominal flow.

**11.4. Validity Flags**

VO, V1

**11.5. Below Method Detection Limit Values**

<b>Substance (wavelength used for calibration)</b>	<b>Method Detection Limit (pg/m<sup>3</sup>) 12 hour sample</b>
4-nitro-phenol (405nm)	10
benzoate (192 nm)	320
2-OH-benzoate (201 nm; peak height)	55
3-OH-benzoate (201 nm)	6.4
4-OH-benzoate (280 nm)	12
4-me-phthalate (199 nm)	6.6
p-phthalate (239 nm)	15
m-phthalate (206 nm)	5.6
o-phthalate (195 nm)	89
1,2,3-bz(COOH) <sub>3</sub> (200nm)	5.9
1,2,4-bz(COOH) <sub>3</sub> (201nm)	8.6
1,2,4,5-bz(COOH) <sub>3</sub> (207 nm)	17

V1 flag will be used.

**11.6. Derived Parameters****11.7. Explanation of Zero or Negative Data****12. Data Quality Objectives (Pre-Study)****12.1. Accuracy**

Total uncertainties (calibration, reproducibility, evaluation) are estimated at:

4-nitro-phenol: 16 %  
benzoate: 16 %  
2-OH-benzoate: 42 %  
3-OH-benzoate: 34 %  
4-OH-benzoate: 36 %  
4-me-phthalate: 32 %  
p-phthalate: 22 %  
m-phthalate: 22 %  
o-phthalate: 30 %  
1,2,3-bz(COOH)<sub>3</sub>: 25 %  
1,2,4-bz(COOH)<sub>3</sub>: 26 %  
1,2,4,5-bz(COOH)<sub>4</sub>: 34 %

**12.2. Precision**

N/A

**12.3. Comparability**

N/A

**12.4. Representativeness**

-Depending on conditions, the measurements at this Sumas site can be representative of processed urban air masses with influence from primary



and secondary biogenic sources. The measurements can also be representative of direct biogenic emissions as the site is in the heart of a mixed forest on Sumas forest at 300m elevation. Daytime measurements will likely be representative of the boundary layer, while night time measurements will likely be decoupled from the valley floor due to the elevation of this site (300m asl).

-The Cassiar samples are representative of direct mobile emissions.

-The measurements at the Slocan Park site will be representative of the typical urban/suburban pollution mix that is not significantly processed photochemically.

-The measurements at the Langley site will be representative of either clean marine air (with southwest flows) or processed air pollution (with northwest flows) in which secondary pollutants will have formed.

**12.5. Completeness**

N/A

**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: