British Columbia Ministry of Water, Land and Air Protection

Golden Source Apportionment Study

Quality Assurance Project Plan

March 2005

Library and Archives Canada Cataloguing in Publication Data

Main entry under title:
Golden source apportionment study : QA/QC plan

"March 2005"
Also available on the Internet.
Includes bibliographical references: p.
ISBN 0-7726-5287-2

1. Air quality management - British Columbia - Golden.
2. Air – Pollution – Measurement – Standards – British Columbia. 3. Air quality - British Columbia – Golden.
4. Air - Pollution - British Columbia - Golden. I. British Columbia. Water, Air and Climate Change Branch. II. Title: Golden source apportionment study : Quality assurance/Quality control plan. III. Title: Quality assurance/Quality control plan.

TD883.148.C3G64 2005 363.739'22'0971168 C2005-960074-8

Table of Contents

List of Figures

List of Tables

List of Equations

List of Acronyms

ADaMS – Air Data Management System

BC – Black Carbon (measured by aethalometer)

CRPAQS – California Regional $PM_{2.5}$/PM_{10} Air Quality Study

DQOs – Data Quality Objectives

DQSRs – Data Quality Summary Reports

EC – Environment Canada

EMS – Environmental Monitoring System

EPA – United States Environmental Protection Agency

ETC – Environmental Technology Center (Environment Canada Laboratory)

FRM – Federal Reference Method

IC –Ion Chromatography

LQL – Lower Quantifiable Limit

NAPS – National Air Pollution Surveillance program (Environment Canada)

OC/EC – Organic Carbon/Elemental Carbon

QA/QC – Quality Assurance/Quality Control

SAS – Statistical Analysis System

SOPs – Standard Operating Procedures

TEOM – Tapered Element Oscillating Microbalance (for continuous monitoring of $PM_{2.5}$ and PM_{10})

UVC - Carbon measured in the UV spectrum on the Dual Channel Aethalometer

WLAP – British Columbia Ministry of Water, Land and Air Protection

WAMR – Water and Air Monitoring and Reporting section (within WALP)

XRF – X-ray Fluorescence

Introduction

The purpose of this document is to provide a QA/QC framework for the Golden source apportionment study 2004-2006. *Quality assurance* (QA) for a field program such as the Golden speciation study integrates *quality control* (QC), audits and measurement validation. QC is intended to prevent, identify, correct, and define measurement difficulties and to provide the QC test data needed to quantify the precision accuracy and validity of the data (Hafner, 2004).

QA/QC protocols are included in this document for all instruments and parameters identified in the study. Most protocols are derived from Environment Canada/NAPS manuals except where EPA and WLAP protocols are more appropriate.

The Golden QA/QC Plan covers four QA/QC Components of the project. These are:

1. QA/QC field features of the Golden Study
    a. Instrumentation co-location
    b. External field audits

2. Standard operating procedures (SOPs) for instruments including:
    a. Instrument operation and handling of filters/cartridges
    b. Calibration and performance tests
    c. Site visitation schedules
    d. Equipment maintenance and repairs
    e. Siting criteria for instruments

3. Data Validation:
    a. WLAP data validation procedures

4. Data Quality Summary Reports (DQSR) for each parameter:
    a. Operating sites and times for each parameter
    b. Data quality objectives
    c. Data recovery and completeness
    d. Lower Quantifiable Limit (LQL)
    e. Accuracy
    f. Precision

This document is intended to compliment the manufacturers' manuals for each instrument. Operators are encouraged to consult the manual where necessary.

Instrumentation and Parameters

Figure 1 is a map of the station locations in Golden. Table 1 below lists the instrumentation used and parameters measured in the Golden study. The dichotomous sampler (2025), speciation monitor (2300) and the TEOM $PM_{2.5}$/PM_{10} are components of the Canada-wide NAPS program. Sampling and preparation of filters and speciation cartridges will be provided by NAPS. All other instrumentation is provided by WLAP.

EC Laboratory Analysis Protocols

Laboratory and analysis protocols are not included in this document but are covered by the NAPS program. Laboratory and speciation method protocols are shown in Appendix 10. NAPS QA/QC procedures for filter mass and chemistry analysis for Dichot and speciation sampler filters include procedures for field and laboratory blanks.

Air Quality Technicians in Golden supply the ETC lab in Ottawa with flow rates and operating times for each filter/speciation cartridge sent out. The Dichot and the speciation monitor are checked quarterly for flow verification.

Quality Assurance/Quality Control Flow Diagram – WLAP Instrumentation (TEOM $PM_{2.5/10}$, Met, BC, O_3, NO_x/NO, SO_2, CO)

Figure 2 is a generalized flow diagram of how the QA/QC components of WLAP's continuous monitoring program in Golden relate to each-other and how data becomes validated for a given parameter.

Standard Operating Procedures for the continuous air quality instruments cover protocols for the station siting, setup and startup. Start-up forms with the station's lat, long, name and parameters measured are sent to the data validation department in Victoria (WAMR) for initiation of the instruments. Raw data is collected automatically via phone line and downloaded onto a central database for validation. Calibration and operator logs (covered under the SOPs for each instrument) are sent to the data validation department and are used to screen the raw data for outliers, missing data and other problems. Further QA checks are performed on the data using results from co-located monitors (e.g. 24hr EC vs. 24hr BC, 24hr TEOM $PM_{2.5}$ vs 24hr Dichot $PM_{2.5}$, Central Golden met vs Northern/Southern met).

After the data is validated, data quality summary reports are created for each continuous parameter after a period of three months of continuous data collection. Data quality objectives for data completeness, accuracy, precision and lowest quantifiable limit (discussed later in this plan) are compared with actual results for each parameter and are summarised in a report.

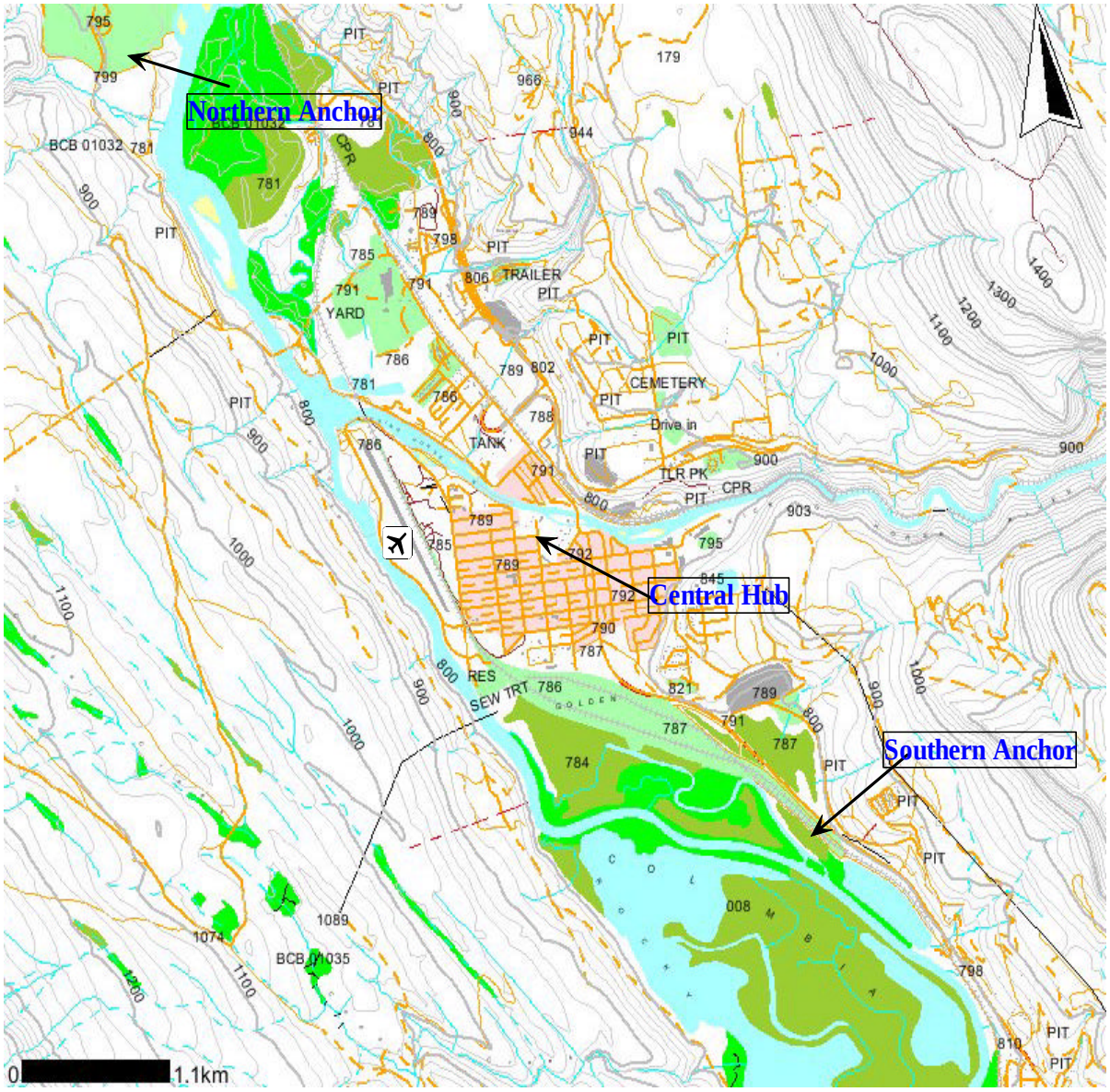


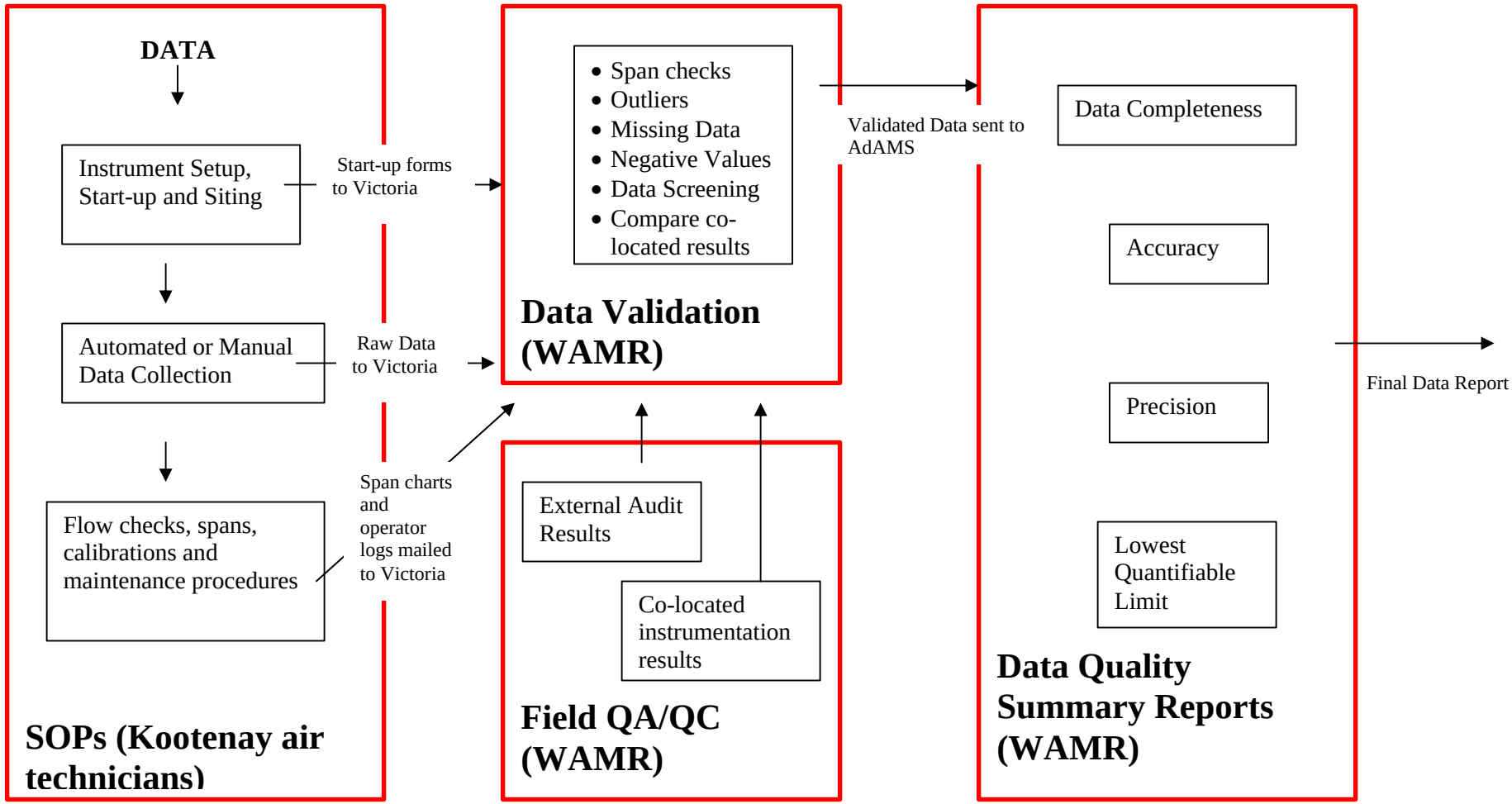
Figure 1 Station Locations (Central Hub = Golden Townsite mobile, Golden Hospital and Lady Grey School; Southern Anchor = Golden CPR site; Northern Anchor = Golden Golf Course).

Table 1. Golden Site and Instrument Details

Site	Instrument	Parameters	Filters/Denuders	Laboratory	Frequency	Duration
Golden Hospital: Durand Manor	$PM_{2.5}$ R&P 2300 speciation monitor	$PM_{2.5}$ ions[1], OC/EC[2], mass for QA/QC check	Teflon, Nylon, Pre-fired quartz, denuders[3]	NAPS-ETC	1-in-3 day and episodic periods (122 days/year)	24-hr
	R&P 2025 plus Dichotomous $PM_{2.5}$/$PM_{2.5-10}$	$PM_{2.5}$/$PM_{2.5-10}$ mass and metals[4], $PM_{2.5-10}$ ions	Teflon	NAPS-ETC	Runs concurrently with 2300 (122 days/year)	24-hr
	R&P 2025 plus Dichotomous $PM_{2.5}$/$PM_{2.5-10}$	$PM_{2.5-10}$ OC/EC	Pre-fired quartz	NAPS-ETC	1-in-3 day episodic periods concurrent with 2300 monitor (30 days/year)	24-hr
Golden Townsite: Mobile Unit	TEOM $PM_{2.5}$ and PM_{10}	$PM_{2.5}$/PM_{10} mass	N/A	N/A	Continuous	5-min/60-min
	O_3 (Telidyne-API)	O_3	N/A	N/A	Continuous	Hourly
	NO_x(Telidyne-API)	NO_x	N/A	N/A	Continuous	Hourly
	SO_2(Telidyne-API)	SO_2	N/A	N/A	Continuous	5-min/60-min
	CO(Telidyne-API)	CO	N/A	N/A	Continuous	Hourly
	Magee AE2 Aethalometer	BC (+UV-C)[5]	N/A	N/A	Continuous	5-min/60-min
Golden: Lady Grey School	Surface met	Wind, Temp, RH	N/A	N/A	Continuous	Hourly
Golden CPR	Magee AE2 Aethalometer[6]	BC (+UV-C)	N/A	N/A	Continuous	5-min/60-min
	TEOM $PM_{2.5}$/PM_{10}	$PM_{2.5}$/PM_{10} mass	N/A	N/A	Continuous	Hourly
	Surface met	Wind, Temp, RH	N/A	N/A	Continuous	Hourly
Golden Golf Course	TEOM $PM_{2.5}$/PM_{10}	$PM_{2.5}$/PM_{10} mass	N/A	N/A	Continuous	Hourly
	Surface met	Wind, Temp, RH	N/A	N/A	Continuous	Hourly

[1] Nitrite, phosphate, fluoride, NO_3^-, SO_4^{-2}, Cl^-, NH_4^+, K^+, Na^+ and Mg^{+2}
[2] EC (Elemental Carbon), OC (Organic Carbon)
[3] NAPS to ship prepared speciation cassettes
[4] Al, Si, P, K, S, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Pb, Na, Mg, Ce, Pr, Nd, W, Hg.
[5] BC – Black Carbon, UV-C – Organic carbon captured in UV spectrum
[6] Backup instrument for Golden Townsite, shared between the Golf Course and the CPR site.

Figure 2. Flow Diagram for QA/QC of Golden continuous data (group responsible in parenthesis)



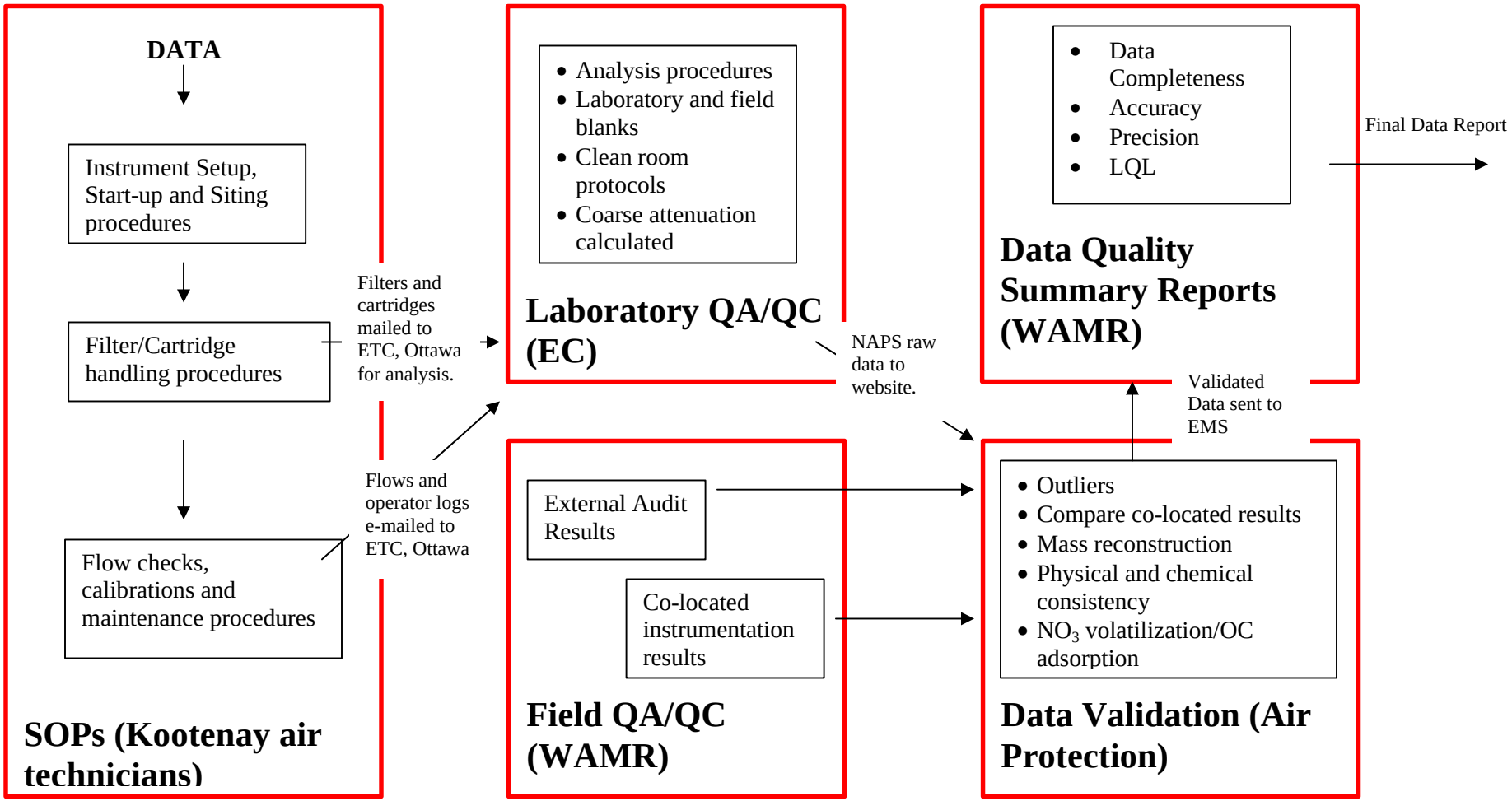
Quality Assurance/Quality Control Flow Diagram – EC/NAPS Instrumentation and Analysis (24hr mass, metals, ions, OC/EC)

Figure 3 is a flow diagram for the 24hr filter based speciation component of the Golden program. Instrumentation (Dichot and speciation monitor) is maintained and calibrated by Kootenay air technicians. Flow and calibration data are sent along with the exposed filters to the ETC lab in Ottawa. Filter pre and post weights and chemical analysis are done at the lab. X-ray results for metals are corrected to account for coarse particle attenuation when analyzing lighter elements by XRF. Data is not validated for outliers or major discrepancies by the laboratory.

The raw data is then deposited on the NAPS web database into two separate folders. The SPECIATION folder contains the major ions and OC/EC data, the DICHOT folder contains the coarse and fine mass, metals and minor ion (K, Na etc…) data. Both files are in .WK1 format which is easily imported into MS Excel.

Raw 24hr data is compared with the continuous data for validation of mass and BC vs. EC. Further validation of the 24hr data is not done by the data validation department but is instead carried out during the initial phase of data analysis. At a minimum, plots are made of the data to determine major outliers or discrepancies. See Section 3 - Data Validation for further details. After validation, the data is then downloaded by WAMR into EMS for storage and analysis. Data quality summary reports are produced for 24 hr $PM_{2.5-10}$ and $PM_{2.5}$ mass only.

Figure 3. Flow Diagram for QA/QC of Golden 24hr speciation data (Laboratory QA/QC not covered in this document).



1. Field QA/QC Features of the Golden Study

There are several field QA/QC features of this study including:

- *Collocation of the dichot (2025) with the speciation monitor (2300) at the Golden Hospital site for QA analysis of metals and mass in $PM_{2.5}$.*
    - EC will analyze both metals and mass on the speciation monitor and the collocated Dichot. The primary mass measurement is the dichot and the speciation mass result will serve as a backup measurement. The agreement will be a useful QA check.
- *Collocation of the $PM_{2.5}$ and PM_{10} TEOMs at the Golden Townsite with the dichot and speciation sampler for $PM_{2.5}$ and PM_{10} mass at the Golden Hospital.*
    - TEOM concentrations will be rolled in to 24hr averages and compared with 24hr values from the non-continuous instruments. Correlation values will be reported in the annual and final reports.
- *Collocation of filter based OC/EC measurements with continuous BC aethalometer.*
    - Previous research (Babich *et al*, 2000) shows good correlation between EC derived on quartz filters using thermal methods and 24hr averages of aethalometer derived BC (~0.92). However, BC is consistently ~25% less than EC for most studies. Results from each method will be compared as a QA check to ensure that both methods are accurately assessing carbon concentrations.
- *Proximity of surface meteorological measurements at the three valley sites to provide data for the comparison of the zone of influence for both meteorology and PM mass.*
    - Meteorological data from the central (Hospital), south (CPR) and north (golf course) sites will be compared over episodic and non-episodic periods to determine wind pattern differences between sites (if any) and the influence of localized meteorology on PM mass.
- *Biannual external audits of instrument siting, operation and procedures*
    - The WLAP external audit team will visit all of the Golden sites to audit the instrument siting, operation (e.g. flow) and technical staff procedures. Sites (instruments) will receive either a pass or fail. If the site fails for calibration reasons, previous data from the instrument is invalidated from the audit date to the last calibration and future data is invalidated until the

next calibration. If the site fails due to physical or maintenance problems (e.g. messiness, unsafe conditions etc…) the data is not invalidated but the operators are given a timeline to correct the problem.

The features listed above will be checked on a routine basis during the data validation process. Where problems arise (e.g. TEOM data does not match FRM-like measurements) actions will be taken to determine if the problem is QA related or random.

2. Standard Operating Procedures and Siting Criteria

All protocols in this study are derived directly from NAPS and are included in the appendices of this document with the exception of:

- Meteorological stations (WS, WD, T, RH) – WLAP provincial siting criteria and manufacturer's manual

- Aethalometer SOP – Washington State Department of Ecology

Tables 2 and 3 provide a summary of the instrument QA/QC procedures and the references to the written protocols.

Table 4 is a brief summary of the siting criteria for each instrument along with references to the complete protocols

Operators are encouraged to consult the manufacturer's manual where necessary.

Table 2. Golden Speciation Program: Particulate and Meteorological Instrumentation Operation Protocols

Instrument	Required Visit	Filter Handling	Leak Check	Flow and Sensor Verification	Flow Calibration	Servicing and Maintenance	External Audit[7]
R&P 2300 Speciation Sampler	1/6 days (Visual inspection)	See Appendix 1 (pg. 2)	1/3 months Appendix 1 (pg. 3)	1/6 months (temp, pressure and flow) Appendix 1 (pg. 3)	1/12 months or as needed. Appendix 1 (pg. 4)	See Appendix 1 (pg. 4)	2/year
R&P 2025 Plus Dichotomous Sampler (Mass, Metals)	1/6 days (Visual inspection)	See Appendix 2 (pg. 2)	1/4 samples Appendix 2 (pg. 3)	1/6 months (temp, pressure, flow) Appendix 2 (pg. 3)	1/12 months or as needed. Appendix 2 (pg. 4)	See Appendix 2 (pg. 4)	2/year
R&P 2025 Plus Dichotomous Sampler (Coarse fraction OC/EC)	1/6 days (Visual inspection)	See Appendix 2 (pg. 2)	1/4 samples Appendix 2 (pg. 3)	1/6 months (temp, pressure, flow) Appendix 2 (pg. 3)	1/12 months or as needed. Appendix 2 (pg. 4)	See Appendix 2 (pg. 4)	2/year
$PM_{2.5}$/PM_{10} TEOM	1/6 days (Visual inspection)	See Appendix 3 (A1-1)	Each sample filter change Appendix 3 (A1-3)	1/6 months (temp, pressure, flow) Appendix 3 (A1-12)	1/12 months or as needed. Appendix 3 (A1-7, 8)	See Appendix 3 (A1- 2, 4, 5, 6)	2/year

Instrument	Required Visit	Wind Speed and Direction Calibration
Surface Meteorology Station (WS, WD, T, RH)	Weekly (visual speed and direction verification)	1/6 months See Appendix 4

[7] Site and instrument audit performed by WAMR's external audit team. Audit based on pass/fail performance.

Table 3. Golden Speciation Program: Gas and BC Instrumentation Operation Protocols

Instrument	Required Visit	Data Set Requirements	Zero and Span Verification	Verification of Operational Parameters	Calibration	Calibration Verification	External Audit
O_3 (Telidyne-API)	1/6 days	500ppb or 1000ppb after installation (refer to manual)	1/6 days Appendix 5 and manual	1/6 days Appendix 5 and manual	After installation or repair and as needed thereafter (Appendix 5 and manual)	1/6 months (Appendix 5 and manual)	2/year
NO_x(Telidyne-API)	1/6 days	Refer to manual	1/6 days Appendix 6 (VI-2) and manual	1/6 days Appendix 6 and manual	After installation or repair and as needed thereafter (Appendix 6 and manual)	1/6 months (Appendix 6 and manual)	2/year
SO_2(Telidyne-API)	1/6 days	5-min sampling frequency MDL = 1 ppb	1/6 days Appendix 6 (VI-2) and manual	1/6 days Appendix 6 and manual	After installation or repair and as needed thereafter (Appendix 6 and manual)	1/6 months (Appendix 6 and manual)	2/year
CO(Telidyne-API)	1/6 days	MDL = 100 ppb	1/6 days Appendix 6 (VI-2) and manual	1/6 days Appendix 6 and manual	After installation or repair and as needed thereafter (Appendix 6 and manual)	1/6 months (Appendix 6 and manual)	2/year

Instrument	Required Visit	Data Set Requirements	Verification of Operational Parameters	Service and Maintenance	Flow Verification	Optical Strip Test	External Audit
Magee AE2 Aethalometer	1/6 days	5-min sampling frequency	1/6 days[8]	See Appendix 7	1/30 days	Not necessary[9]	2/year

[8] Operational parameters on the aethalometer include screen flow rate, filter check (for tearing) and screen time check. Screen time on the aethalometer should be within ± 30 seconds of the verified ADaMS time (set to atomic clock).

[9] The optical strip test is not recommended by the manufacturer. Flow rate verification is most important for QA/QC.

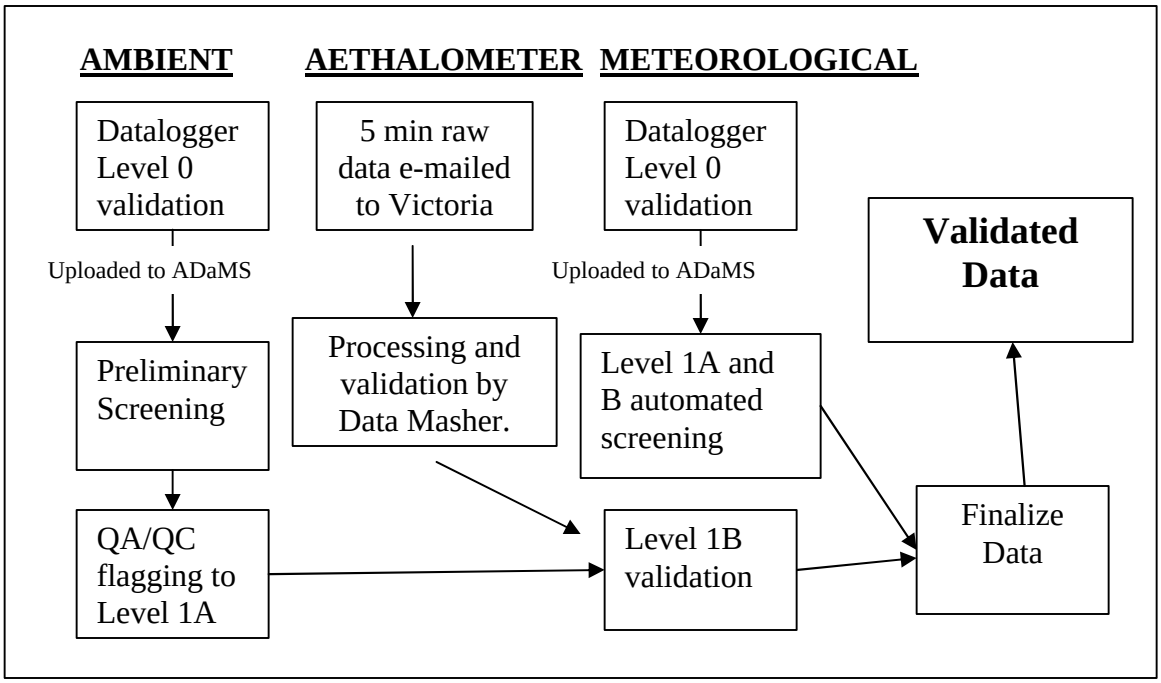
Table 4. Golden Speciation Program: Instrumentation Probe Siting Criteria

		Distance From Supporting Structures (m)		
Instrument	**Height Above Ground (m)**	**Vertical**	**Horizontal**	**Other Spacing Criteria**
R&P 2300 Speciation Sampler	2 - 15		>2	Same as TSP (Appendix 6, pg 9 – 17)
R&P 2025 Plus Dichotomous Sampler (Mass, Metals)	2 - 15		>2	Same as TSP (Appendix 6, pg 9 – 17)
R&P 2025 Plus Dichotomous Sampler (Coarse fraction OC/EC)	2 - 15		>2	Same as TSP (Appendix 6, pg 9 – 17)
$PM_{2.5}$/PM_{10} TEOM	2 - 15		>2	Appendix 6, pg 9 – 17, Appendix 3, sect. 2
Surface Meteorology Station (WS and WD)	10m minimum	> 1 m above roof-top circulation cavity	>10x ht. of obstruction	Appendix 8, pg 6
Surface Meteorology Station (T and RH)	1.2m minimum	> 1 m above roof-top circulation cavity	>2x ht of nearest obstacle	Appendix 8, pg 7
O_3 (Telidyne-API)	2 - 15	>1	> 2 or 2x ht of obstacle above inlet	Appendix 5, sect. 8. Appendix 6, pg 9 - 17
NO_x(Telidyne-API)	3 - 15	>1	>1	Appendix 6, pg 9 - 17
SO_2(Telidyne-API)	3 - 15	>1	>1	Appendix 6, pg 9 - 17
CO(Telidyne-API)	3 - 5	>1	>1	Appendix 6, pg 9 - 17
Magee AE2 Aethalometer	Should be level with SO_2	Should be level with SO_2	Should be level with SO_2	Appendix 7, pg 56 - 57

3. Data Validation Procedures

The WAMR data validation team validates all of the continuous air monitoring data coming into the provincial database. 24hr filter based data is validated by the laboratory and the Air Protection section of WLAP. Validation of continuous data occurs monthly for ambient continuous data using the QA/QC validation program in ADaMS as well as strip charts, span reports and printed data reports. Aethalometer data is downloaded off of a floppy disk from the instrument every week and e-mailed to Victoria where is processed and validated using the Data Masher program from WUAQL. Meteorological data is automatically validated nightly using a SAS program. Figure 4 shows the validation process for continuous ambient and meteorological data.

Figure 4. Flow Chart for data validation procedures



Ambient Data

Level "0" data[10] are acquired from dataloggers and automatically uploaded to a central database (ADaMS) for validation in Victoria. Ambient data is captured by the data validation team and a preliminary screen is performed and data results are rounded to 2 decimal places. Once per month the data is printed off as a preliminary report and reviewed. Preliminary reports contain daily mean and maximum concentration as well as the monthly mean and the percent valid data. Data is then routed through the QA/QC

10 These data are obtained directly from the data loggers that acquire data in the field. Averaging times represent the minimum intervals recorded by the data logger, which do not necessarily correspond to the averaging periods specified for the database files. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline and span changes been applied (Hafner, 2004).

program where suspect or invalid data is flagged and the results are rounded to 1 decimal place. Calibration (for gases only) and strip charts are reviewed for each instrument to assess the level of data noise and baseline drift. Audit results are also reviewed. Initial QA screening to level "1A"[11] is performed using a combination of 1) the QA/QC screening tool which flags data with one of 5 flags (F- Failure, B- Out of range, H- Data higher than normal, D- Instrument downtime, C – Daily span calibration for gases) and 2) visual verification of outliers using graphing tools in ADaMS and 3) verification of data using strip charts, preliminary reports, calibration reports, power failure reports and audit results for each instrument.

During the screening TEOM $PM_{2.5}$ and PM_{10} data is corrected for negative values. For $PM_{2.5}$ values between -3.4 and 0 are adjusted to 0, values less than -3.5 are invalidated. For PM_{10} values between -9.8 and 0 are adjusted to 0, values less than -9.9 are invalidated.

Data can be invalidated for one or a combination of the following:

1. Malfunction of the instrument
2. Baseline drift greater than 3% of Full Scale (using strip charts)
3. Noise level greater than 2% of Full Scale.
4. Span drift greater than 10% deviation from that established during an audit or calibration
5. Leak in sampling system.
6. $PM_{2.5}$ data < -3.5 $\mu g/m^3$
7. PM_{10} data < -9.9 $\mu g/m^3$
8. Data completeness < 50 min/hr or 4 min/5min
9. Failed audit.
10. Unsatisfactory calibration results.
11. Slow response, i.e. response time during span check, calibration check or audit is greater than 20 minutes.
12. Suspected loss of sample in instrument due to contamination
13. Failure of the thermal oxidizer
14. Failure of the scrubber material.

Data is further validated to level "1B"[12]. Data can be classified as suspect requiring further investigation for the following reasons:

11 These data have passed several validation tests applied by the measurement expert prior to data submission. The general features of Level 1A are (1) flagging and removal of data values and replacement with -999 when monitoring instruments did not function within procedural tolerances; (2) flagging measurements when significant deviations from measurement assumptions have occurred; (3) verifying computer file entries against data sheets; (4) replacing data from a backup data acquisition system in the event of failure of the primary system; (5) adjusting measurement values for quantifiable baseline and span or interference biases; and (6) identifying, investigating, and flagging data that are beyond reasonable bounds or that are unrepresentative of the variable being measured (Hafner, 2004).

12 These data have met consistency tests to verify that file naming conventions, data formats, site codes, variable names, reporting units, validation flags, and missing value codes are consistent with project conventions. When the received files are consistent, reasonability tests are applied that include identifying data values that (1) are outside of a specified minimum or maximum value; (2) change by more than a specified amount from one sample to the next; and (3) do not change over a specified period. Data identified by these filters are individually examined and verified with the data supplier.

1. Results appear abnormally high.
2. Abnormal rate of change (e.g. >50 µg/m^3 over several minutes).
3. Data appears "stuck" (e.g. $PM_{2.5}$ >50 µg/m^3 for more than 5 hours)
4. Co-located FRM mass does not agree with 24hr TEOM results.

Table 5 gives examples of useful time series plots used in level 1B data validation of continuous $PM_{2.5}$/PM_{10} and gaseous data.

Table 5. Useful time series plots of $PM_{2.5}$ and gases for data validation (and analysis)

Species	**Expectation/Action**
All continuous data	Diurnal variability consistent with meteorology and nearby sources.
All continuous data	Spikes not concurrent with any other parameter are flagged as suspect.
All continuous data – baseline inspection	No step or steady-over-time changes in the lowest concentrations during the sampling period.
NO and Ozone	Dips in ozone may be accompanied by increase in NO.

Data flagged as suspect is reviewed using the one-minute data to check for outliers and trends. Data is invalidated if instrument failure or other operational problems are the reason. Episodic data due to naturally occurring events is not invalidated (e.g. forest fires, thermal inversions). In cases other than obvious instrument failure or calibration problems, there are no set rules for the invalidation of data. In cases where data appears suspicious, tools such as time series graphs of the 1-minute data and comparing with co-located results are used to determine the cause of the abnormality.

The decision to invalidate or not is left to the judgement of the data validation personnel. For this reason, data validation is performed by an air pollution professional with intimate knowledge of the sensors, recording system and air pollution problems.

Refer to Appendix 9 – Continuous Air Analyzer Data Interpretation Guidelines for further details on WLAP validation procedures.

Aethalometer Data

Data from the aethalometer is written to an internal floppy disk in five minute sampling periods. Data includes time, date, BC concentration (ng/m^3), UV+BC concentration and average flow (L/m). One file is created for every sampling day. Data from the floppy

Obvious outliers (e.g., high solar radiation at midnight, 300°C temperature) are invalidated. Others may be invalidated or flagged based on the results of the investigation.(Hafner, 2004)

disk is downloaded every week and e-mailed to Victoria for compilation and validation. Using the Data Masher program the files are compiled every 3 months into 1 file and the data is rolled up into hourly averages. Level 1A validation is performed on both the hourly and five minute data automatically. The program checks for suspect and invalid data using the following criteria (WUAQL, 2003):

1. Data and time format and time stamp are correct
2. "Lamp On" voltage is >0.35V and < 1.5V
3. Missing data assigned null value
4. BC 5-minute value must be > -10 $\mu g/m^3$.
5. BC and UV 1hr data must be > -0.3 $\mu g/m^3$.
6. Flag 1hr data with one or more 5min data point voided.

Recorded flow rates are also checked and data are voided with > 10% discrepancy in flow rate between five minute intervals.

Validation to level 1B is done with the quarterly compiled data and includes checks for sticking, abnormal rates of change (spikes), unusually high results, 24hr EC mass does not agree with 24hr BC mass and 24hr BC mass is = than 24hr collocated $PM_{2.5}$. See Table 6 for details.

Table 6. Useful plots for Aethalometer data validation (and analysis)

Species	**Species**	**Expected Relationship**	**Source/Reason**
Hourly BC	Hourly $PM_{2.5}$	Correlation	Correlation of 0.5 – 0.9 expected, investigate outliers.
Hourly UVC - BC	Hourly $PM_{2.5}$	Some correlation	Correlated points indicate high wood smoke periods
Hourly UVC	Hourly BC	Correlation	Well correlated during low wood smoke periods, poorly correlated during high wood smoke periods
Hourly BC	Hourly $PM_{2.5}$	Time series relationship	Should show similar diurnal variability, hourly spikes in BC not concurrent with $PM_{2.5}$ are suspect.
5min BC	5min SO_2	Some correlation	Differentiate gas/diesel sources
Hourly BC	Hourly NO_x	Some correlation	Previous studies show r^2=0.75
24hr BC	24hr EC	Correlation	r^2 = 0.76 – 1.00 from previous studies

Meteorological Data

Continuous meteorological data is acquired from dataloggers and downloaded to the central database in Victoria (ADaMS). Data is validated nightly using a SAS program

which screens the data for 22 criterions for wind speed, wind direction, temperature and relative humidity. If data does not meet specific criteria an e-mail message is mailed to the data validation staff for further investigation.

Table 7 is the screening criteria for meteorological data.

24hr Speciation Data

Raw 24hr data is compared with the continuous data for validation of mass and BC vs. EC. Further validation of the 24hr data is not done by the data validation department but is instead carried out during the initial phase of data analysis. At a minimum, plots are made of the data to determine major outliers or discrepancies. Chemical consistency of the results is checked (e.g. sulphur vs. sulphate, chloride vs. chlorine etc…). Table 8 shows a list of useful scatter plots used to validate the $PM_{2.5}$ speciated data.

Mass reconstruction is also used to compare the sum of analytes with the actual determined mass. Mass reconstruction attempts to reconstruct the PM mass using the sum of all analytes. Constant factors account for total molecule mass (e.g. O_2 in $CaCO_2$). The equation for reconstructed fine mass (RCFM) is shown below

Equation 1. Mass Reconstruction of $PM_{2.5}$

RCFM = Ammonium Sulfate + Ammonium Nitrate + Organic Carbon (OC) + EC + SOIL + other analytes

$RCFM = 4.125*S + 1.29*NO_3 + 1.4*OC + EC + (2.2*Al + 2.49*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti + 1.41*K) + 1.79*V + 1.24*Zn + 1.12*Ba + Mg + Na + Ni + Cu...$

Table 7. Data Validation Criteria for Meteorological Parameters

	Validation Criteria			
Parameter	**Description**	**Range**		**Validation Rules**
		Minimum	Maximum	
TEMP_MEAN	Mean Temperature	-40.0	40.0	If difference greater than 5 °C from the previous hour then flag data. If the difference between 24 consecutive hours less than 0.5°C then flag data.
TEMP_MIN	Minimum Temperature	-40.0	40.0	If difference greater than 5 °C from the previous hour then flag data. If the difference between 24 consecutive hours less than 0.5°C then flag data.
TEMP_MAX	Maximum Temperature	-40.0	40.0	If difference greater than 5 °C from the previous hour then flag data. If the difference between 24 consecutive hours less than 0.5°C then flag data.
WSPD_SCLR	Mean Wind Speed	0	25	If difference for three consecutive hours is less than 0.1 m/s then flag data. If the difference for 12 consecutive hours is less than .5 m/sec then flag data. If three hours less than 0.1 m/sec then check for calm. If temperature > 2 and sigma=0 then calm detected. If temperature between –2 and 2 then possible frozen sensor
WSPD_VECT	Mean Wind Vector Magnitude	>0	25	This should always be less than Mean Wind Speed (WSPD_SCLR)
WDIR_VECT	Mean Wind Vector Direction	0	355	If variance between six consecutive hours is less than 1 degree then flag data. If it does not vary by more than 10 degrees for 18 consecutive hours then flag data.
WDIR_UVEC	Hourly Unit Vector Wind Direction	0	355	Same as for Mean Wind vector Direction.
SIGM_15MIN	Pseudo Hourly Sigma Theta	>0	30	

TEMP_DELT	Hourly Delta Temperature	> -3.0	< 5.0	The value must be greater than 0.1°C/m during daytime The value must less than 0.1°C/m during night time
SIGM_ALL	True Hourly Sigma Theta (All Values)	>0		Always larger than Pseudo Hourly Sigma Theta SIGM_15MIN
SIGM_ALLP	True Pseudo Hourly Sigma Theta	>0	30	If difference between six consecutive hours < 1.5 degrees then flag data
WSPD_3SEC	Maximum 3 Sec Gust Over One Hour	>0	50	Always greater than the one hour average wind speed. Always greater than the 1 minute average wind speed.
WSPD_1MIN	Maximum 1 Min. Gust Over One Hour	>0	50	Less than three second gust but greater than one hour average wind speed.
WDIR_U1MIN	Unit Vector Direction (1 Min. Gust)	>0	355	
TIME_3SEC	Time of Gust(WSPD_3SEC)	0	2359	If not valid time delete
SIGM_WSPD	Standard Deviation of Wind Speed	0	30	If value is not zero value should be greater than 1
BATT_VOLT	Data logger Battery Voltage	11.76	16.0	Email Message if out of range
PGM_VER	Data logger pgm version	same as prev.		Email Message if pgm version has changed
PGM_SIG	Data logger pgm signature	same as prev.		Email Message if pgm signature has changed
CAP_PER (15 min.)	% uptime for interval			Must be 95 percent or greater for each quarter
CAP_PER (60 min.)	% uptime for interval			Must have three valid quarters for valid measurement. Temperature requires all four quarters
HUMIDTY	% relative humidity	>0	< 100	

Table 8. Example of useful scatter plots of $PM_{2.5}$ data for validation (and analysis).

Species	Species	Expected Relationship	Source/Reason
SO_4^-	S	3*S ~ SO_4^-	IC vs. XRF
Cl^-	Cl	~1:1	IC vs. XRF
Na^+	Na	~1:1	IC vs. XRF
K^+	K	~1:1 (unless K is predominantly crustal derived)	IC vs. XRF
Na	Cl	Correlation	Sea salt, road salt
Na, Mg, Ca	Cl	Possible Correlation	Road salt- dependent on type of salt used e.g. MgCl, NaCl, CaCl.
Ca	Si	Correlation	Soil
Al	Si	Correlation	Soil
Fe	Si	Correlation	Soil
Fe	K	Correlation	Soil
OC	TC	Correlation	OC generally a large fraction of TC
EC	TC	Some Correlation	EC a part of TC
BC	EC	Correlation	r^2 = 0.7 – 1.00
Se	SO_4	Some Correlation	Coal emissions
Fe	Zn	Some Correlation	Smelter emissions
Ni	V	Some Correlation	Oil combustion
K	EC	Likely bifurcation	Correlated points due to smoke
Cations (K^+, Na^+, NH_4^+)	Anions (Cl^-, NO_3^-, SO_4^-)	~1:1	Aerosol should be neutralized
$PM_{2.5}$	Reconstructed Fine Mass (RCFM)	Good correlation	Reconstructed mass should be ~ equal to $PM_{2.5}$, points not correlated are suspect
$PM_{2.5}$	PM_{10}	$PM_{2.5}$ = PM_{10}	Investigate outliers

4. Data Quality Summary Reports

Data quality summary reports (DQSRs) will be prepared for each continuous parameter as well as $PM_{2.5}$ and PM_{10} filter based mass every year of data collection. The purpose of a DQSR is to provide data users with information on the specifications of data quality including the following information (from Hafner et al., 2003):

- Operating sites and times for a parameter's measurement
- Data quality objectives
- Data recovery and completeness
- The lower quantifiable limit (LQL)
- Accuracy
- Precision

Data Quality Objectives (DQOs)

DQOs address goals for completeness, LQL, accuracy, and precision. Table 9 shows the DQOs for the Golden project and the list of references for each objective. All DQOs for this project are taken from CRPAQS, 2002.

Table 9. Data Quality Objectives for Golden Project

Parameter	Data Completeness[13]	LQL	Accuracy	Precision	Reference
$PM_{2.5}$ Filter Mass (24hrs)[14]	> 85%	2µg/m^3	3%	2µg/m^3	CRPAQS A.13 (DRI)
$PM_{2.5-10}$ Filter Mass (24hrs)	> 85%	2µg/m^3	3%	2µg/m^3	CRPAQS A.13 (DRI)
$PM_{2.5}$ TEOM Mass (hourly)	> 50 min/hr (85%)	5 µg/m^3	3 %[15]	5 µg/m^3	CRPAQS Appendix H
PM_{10} TEOM Mass (hourly)	> 50 min/hr (85%)	5 µg/m^3	3 %[16]	5 µg/m^3	CRPAQS Appendix G
O_3	> 50 min/hr (85%)	1 ppb	3 ppb (10%)	1 ppb	CRPAQS Appendix B
NO	> 50 min/hr (85%)	0.02 ppb	0.05 ppb (10%)	0.02 ppb	CRPAQS Appendix D
CO	> 50 min/hr (85%)	100 ppb	3%	100 ppb	n/a[17]

[13] Data completeness objectives based on WLAP validation protocols of < 10 min missing per hour. 60 minute concentrations with more than 10 minutes missing are invalidated. This corresponds to an approximate objective of 85%.
[14] LQL for 24hr samples based on MDL for mass.
[15] Based on flow rates
[16] Based on flow rates
[17] Based on review of CO data in BC.

SO_2 (hourly and5min)	> 50 min/hr and > 4 min/5 min (85%)	0.2 ppb	0.2 ppb (10%)	0.2 ppb	CRPAQS Appendix C
BC (hourly and 5 min)	> 50 min/hr and > 4 min/5 min (85%)	0.035 µg/m^3	3%[18]	0.035 µg/m^3	CRPAQS Appendix E
Wind Speed	> 50 min/hr (85%)	n/a	n/a	n/a	n/a
Wind Direction	> 50 min/hr (85%)	n/a	n/a	n/a	n/a
Temperature	> 50 min/hr (85%)	n/a	n/a	n/a	n/a
RH	> 50 min/hr (85%)	n/a	n/a	n/a	n/a

Data Completeness

Data completeness quantifies the percentage of valid data points. Data completeness is the ratio of the number of valid data points to the number of captured data points. For each site and parameter, the following quantities will be summarized

- The number of sampling periods for the date range (i.e. the expected number of samples).
- The total number of samples captured.
- The numbers of valid, invalid, suspect and missing samples.

The DQO for data completeness is 85% captured/expected and 85% valid /captured for all meteorological and ambient parameters. This roughly corresponds to the WLAP protocol whereby hourly data with greater than 10 minutes missing per hour is invalidated.

Lower Quantifiable Limit

The LQL is the lowest concentration in ambient air that can be measured when processing actual samples (Hafner, 2004). Sources of variability that influence the monitored signal at low concentrations include instrument noise and atmospheric variability. As a measure of this variability, two times the standard deviation of selected data can be used to estimate the LQL. The selected data will be collected during periods when concentrations are close to the background level and are relatively stable (as measured by a rolling standard deviation). Refer to Table 6 for a list of the LQL objectives for each parameter.

Accuracy

Accuracy is how close the measurements are to the real number. Calibration data are needed to assess accuracy. Accuracy for gaseous parameters (O_3, CO, NO, NO_x, and SO_2) is based on daily span checks comparing the instrument reading with the known span value. Because the TEOM and the Aethalometer have no span capability, accuracy

[18] Based on flow rates

for these instruments is assessed by comparing the flow results from multi-point calibration checks versus the instrument's stated flow. Since flow is the most crucial factor determining accurate measurement of PM and BC it is an adequate surrogate for span values. Accuracy will be calculated for the 24hr mass samples from replicate laboratory analysis results in addition to the flow calibration tests.
Refer to Table 6 for a list of the accuracy objectives for each parameter.

Precision

Precision is confidence in the measurement which can be estimated by repeated measurements or duplicate analyses (Hafner, 2004). Precision for gaseous parameters will be based on comparisons between the daily span concentration and the average span concentration for the study period. For TEOM $PM_{2.5}$ and PM_{10} as well as BC precision will be estimated by evaluating the variance of the pollutant concentrations during periods of low variability when atmospheric influence on variability is assumed to be minimal. This period will have concentrations well above the LQL. Precision will be calculated for the 24hr mass samples from replicate laboratory analysis results in addition to the flow calibration tests.

References

Babich, P., Davey, M., Allen, G. and Koutrakis, P. (2000) *Method Comparisons for Particulate Nitrate, Elemental Carbon and $PM_{2.5}$ Mass in Seven U.S. Cities.* Journal of Air and Waste Management, 50:1095-1105.

Desert Research Institute (2003) *Standard Operating Procedure for Routine Operation of the Sequential Filter Sampler(SFS).* Appendix A.13 in CRPQS. WWW document. http://www.arb.ca.gov/airways/Documents/preliminary/STI/AppA13.pdf

Hafner, H. (2004) *Golden BC $PM_{2.5}$ Source Apportionment Study: Review and Recommendations.* Prepared for: BC Ministry of Water, Land and Air Protection. Technical Memorandum. STI-904050-2496-TM.

Hafner, H., Hyslop, N. and Green, C. (2003) C*alifornia Regional PM_{10} /$PM_{2.5}$ Air Quality Study (CRPQRS) Management of anchor site data.* Prepared for the San Joaquin Valleywide Air Pollution Study Agency. Final Report. STI-999242-20487-FR

Hyslop, N. Brown, S., Gorin, C. and Hafner, H. (2003) *California Regional PM_{10}/$PM_{2.5}$ Air Quality Study (CRPQRS) Data Quality Summary Reports.* . Prepared for the San Joaquin Valleywide Air Pollution Study Agency. Final Report. STI-99924-2310-FR. Appendices B, C, D, E, G, and H.

Washington University Air Quality Laboratory – WUAQL (2003). User Guide for the AethDataMasher – version 4.2g. WWW document: http://www.seas.wustl.edu/user/jrturner/aethalometer/WUAQL_AethDataMasher4.2g_Manual_031120.pdf