# QUALITY ASSURANCE PROJECT PLAN

# AIRCRAFT MEASUREMENTS IN SUPPORT OF TEXAQS II

July 11, 2006

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Title and Approval Sheet

**Preface**
This Quality Assurance Project Plan is submitted in fulfillment of the following quality assurance project plan requirements of the H63 project for the Houston Advanced Research Center (HARC).

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**Quality Assurance Project Plan Approval Sheet**

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# 1. PROJECT DESCRIPTION AND OBJECTIVES

## 1.1 STUDY PURPOSE

During the 2006 Texas Air Quality study, the Baylor University Aztec aircraft will provide observations of ozone, nitrogen oxides, volatile organic compounds, and meteorological parameters to augment and extend the observations of the NOAA Earth System Research Laboratory (ESRL -- which will deploy a Twin Otter for this study). During the experiment, some flight hours will be dedicated to examine specific air quality objectives of interest to local air quality officials and researchers. These flight hours will be flown primarily in the Houston area. The Baylor aircraft will deploy to Houston for 50 flight hours. The research Tasks for the NOAA Twin Otter and the Baylor Aztec are the following:

1. Evaluate daily forecast and propose daily missions based on weather conditions, absence or presence of plumes transported into the region, overlap with other platforms and potential for joint missions, and progress in developing scientific objectives. NOAA scientists, in consultation with TCEQ, HARC, and Baylor investigators will, on a daily basis, specify mission objectives, develop flight plans, and examine potential missions for the next two or three days.
2. NOAA will apply 25 flight hours and Baylor will apply 50 flight hours to missions with the following research objectives:
    a. Investigate the chemistry and dynamics near stationary fronts and the impact of stationary fronts on local air quality
    b. Examine transport into Houston and net production into the area by flying box patterns around the urban region
    c. Examine export of pollution from Houston, including the effects of nocturnal transport and morning PBL entrainment
    d. Investigate PBL evolution and the role of the sea breeze, focusing on the area near the Gulf of Mexico and Galveston Bay.
    e. Fly over the Moody Tower and Williams Tower in situ sites to investigate variations of ozone and aerosol pollution with height and examine vertical diffusion, evolution of the PBL, and formation and role of the nocturnal jet in the transport of pollutants.
    f. SOF instrument evaluation over the Ship Channel (Baylor only).
    g. SOF instrument evaluation near Sweeney (Baylor only).
3. Analyze the observations and present research findings to the Houston air quality community through reports, presentations, and/or scientific papers.

## 1.2 SITE AND ENVIRONMENTAL SYSTEM TO BE TESTED

Flights will occur primarily in the Houston area. The Baylor University Institute for Air Science's Aztec aircraft will provide *in situ* observations of ozone, nitrogen oxides, volatile organic compounds, and meteorological parameters to augment and extend the remotely sensed NOAA observations.

## 1.3 PROJECT OBJECTIVES

**Primary Objectives:**

- Investigate the chemistry and dynamics near stationary fronts and the impact of stationary fronts on local air quality, including the effects of both horizontal stagnation and isentropic subsidence from aloft
- Examine transport into Houston and net production into the area by flying box patterns around the urban region.
- Examine export of pollution from Houston, including the effects of nocturnal transport and morning PBL entrainment.
- Investigate PBL evolution and the role of the sea breeze, focusing on the area near the Gulf of Mexico and Galveston Bay.
- Fly over the Moody Tower and Williams Tower in situ sites to investigate variations of ozone, CO, and aerosol pollution with height and examine vertical diffusion, evolution of the PBL, and formation and role of the nocturnal jet in the transport of pollutants.
- Solar Occultation Flux (SOF) instrument evaluation over the Houston Ship Channel.
- SOF instrument evaluation near Sweeney.

# 2. PROJECT ORGANIZATION

## 2.1 KEY POINTS OF CONTACT

- HARC – Project Manager
  Eduardo Olaguer

- Baylor University - Principal Investigator
  Maxwell E. Shauck

## 2.2 QA MANAGERS

Baylor University: Max Shauck, Grazia Zanin, Theresa Williams, Sergio Alvarez

Air Quality Design, Inc: Martin Buhr

## 2.3 PROJECT PARTICIPANTS AND RESPONSIBILITIES

### 2.3.1 Texas Environmental Research Consortium (TERC)

Project Coordination and Customer [Eduardo Olaguer]:

- Allocates adequate resources to ensure completion of the project in compliance with the stated objectives;
- Provides resources for meeting the project objectives.

### 2.3.2 Baylor University

Project coordinator [Grazia Zanin]:

- Coordinates the contract and budget issues for the Baylor portion of the project;
- Coordinates the field operations of the aircraft and air monitoring equipment;
- Manages Baylor aircraft and data processing personnel;
- Coordinates the development and maintenance of the Baylor portion of project related planning tools (e.g. QAPP, SOPs, etc.);

- Facilitates communication of related information between Baylor and other project participants;
- Provides deliverables from Baylor, to HARC
- Provides project status reports from Baylor to HARC contract manager; and
- Participates in Flight Planning Teleconferences.

Aircraft operations personnel [Maxwell Shauck, Pilot; Darryl Banas, Mechanic]:

- Maintains and operates aircraft in compliance with appropriate FAA regulations;
- Maintains aircraft related flight records and support documentation;
- Coordinates with HARC to determine flight patterns, location and timing to meet project objectives; and
- Participates in Flight Planning Teleconferences.

Measurement systems operations personnel [Sergio Alvarez and Levi Kauffman]:

- Operates and maintains monitoring and sampling equipment according to the QAPP;
- Performs scheduled calibrations and quality control checks on sampling and measurement equipment in compliance with the QAPP;
- Maintains flight records and measurement support documentation;
- Assists the QA personnel with performance evaluations; and
- Participates in Flight Planning Teleconferences.

Data processing personnel [Martin Buhr and Evan Owen]:

- Coordinates the validation, analysis, management, and delivery of aircraft collected data according to the QAPP requirements;
- Helps coordinate the development and maintenance of the Baylor portions of project related planning tools (e.g. QAPP, SOPs, etc.);
- Coordinates development of graphical and non-graphical analysis products for aircraft based flight data;
- Responsible for the development of data and graphical products resulting from project activities;
- Provides other professional engineering services and technical assistance, as needed; and
- Participates in Flight Planning Teleconferences as necessary.

Contracts and budget management personnel [Office of Sponsored Programs, Baylor]:

- Manages contract development; and
- Monitors contract implementation;

# 3. EXPERIMENTAL APPROACH

## 3.1 GENERAL APPROACH AND CONDITIONS

The project objectives will be accomplished using the Baylor Piper Aztec aircraft with the measurement system listed in Section 3.5.

### 3.1.1 Piper Aztec N6607Y

A Piper Aztec will be used to carry all the required measurements. This aircraft has the following operating properties:

Sampling Speed: 90 - 160 knots (46 – 82 m/s)
typical:120 knots (63 m/s)

Endurance at 120 knots:
~7 hours with 30 minute reserve

Instrument package max weight: ~640 lbs

Electrical Power:
two 1 kW sine wave static inverters

Seating Capacity: 1 pilot and 1 scientist

## 3.2 SAMPLING STRATEGY

Presented in Section 4

## 3.3 SAMPLING AND MONITORING POINTS

Presented in Section 4

## 3.4 FREQUENCY OF SAMPLING

Presented in Section 4

### 3.5 MEASUREMENTS

The measurement systems that will be used aboard the Aztec are listed in Table 3-1 and are discussed in Section 5.

Table 3-1.Table of measurements and instruments

| Species/Measurement | Analytical Technique | Detection Limit | Recording Frequency |
|---|---|---|---|
| Ozone ($O_3$) | UV Photometry | 2 ppbv | 1 Hz |
| Sulfur Dioxide ($SO_2$) | Pulsed Fluorescence | 0.5 ppbv | 1 Hz |
| Total Reactive Nitrogen (NOy) | Chemiluminescence | 0.4 ppbv | 1 Hz |
| Nitric Oxide (NO) | Chemiluminescence | 1 ppbv | 1 Hz |
| Nitrogen Dioxide ($NO_2$) | Chemiluminescence with Photolytic ell | 0.2 ppbv | 1 Hz |
| Carbon Monoxide (CO) | Vacuum ultraviolet (VUV) Fluorescence | <20 ppbv | 1 Hz |
| Formaldehyde (HCHO) | Hantzsch reaction and Fluorescence | <0.1ppbv | 90 s |
| Light Scattering ($b_{sp}$ X $10^{-4}$ $m^{-1}$) Red, Green and Blue Wavelengths | 3 λ Nephelometry | 1 x $10e^{-6}$ $m^{-1}$ | 1 Hz |
| Position (Lat, Lon, altitude), RH, temperature, pressure, wind direction, wind speed, turbulence, pitch angle, roll angle, angle of attack, side slip | 2 GPS antennae, transducer, accelerometers, Platinum RTD, RH sensor | Varies with parameter | 1 Hz |

### 3.6 PLAN FOR EVALUATING PROJECT OBJECTIVES

Presented in Section 7

# 4. SAMPLING PROCEDURES

## 4.1 METHOD TO ESTABLISH STEADY-STATE CONDITIONS

Air sampling will be conducted at the nominal cruising speed of 63 m/s.

## 4.2 SITE SPECIFIC FACTORS

Operations from aircraft encounter different measurement issues as compared to those encountered by ground monitors. The sampling equipment inlets installed on the aircraft are situated outside the prop-wash and engine exhaust paths to avoid potential contamination while in-flight. Additional considerations arise from the fact that ambient temperature, relative humidity and pressure can vary greatly during the course of a flight. To account for these issues the aircraft is air-conditioned on the ground to avoid instrument overheating. Temperature, relative humidity and pressure corrections are applied to the flight data and to correct for non-standard operating conditions.

## 4.3 SITE PREPARATION

The aircraft will be operated and maintained in accordance with all applicable federal aviation regulations (FAR). Additionally, all instrumentation and equipment installations will receive approval from the FAA (Federal Aviation Administration) in accordance with applicable FARs.

## 4.4 SAMPLING PROCEDURES

### Gas inlet manifold

The gas-phase instruments share a common manifold and inlet system that facilitates standard addition calibrations. The system is comprised of a ¾ inch OD PFA Teflon inlet tube, positioned forward in the free air about 6 inches from the fuselage wall. This inlet is connected using PFA Teflon fittings to a PTFE Teflon manifold. Each of the gas measurements has separate sampling ports on the manifold with the exception of $SO_2$ and $O_3$ which share a port. The excess flow from the PTFE manifold is directed to a TSI thermal mass flow meter. A PFA Teflon fitting is used to allow the injection of a known amount of calibration gas to the ¾ inch inlet tubing approximately 3 feet upstream of the common manifold. This fitting, in concert with the mass flow meter, allows standard addition calibrations of the various instruments except ozone during flight. A sketch of the inlet manifold is shown below in **Figure 4-1**.

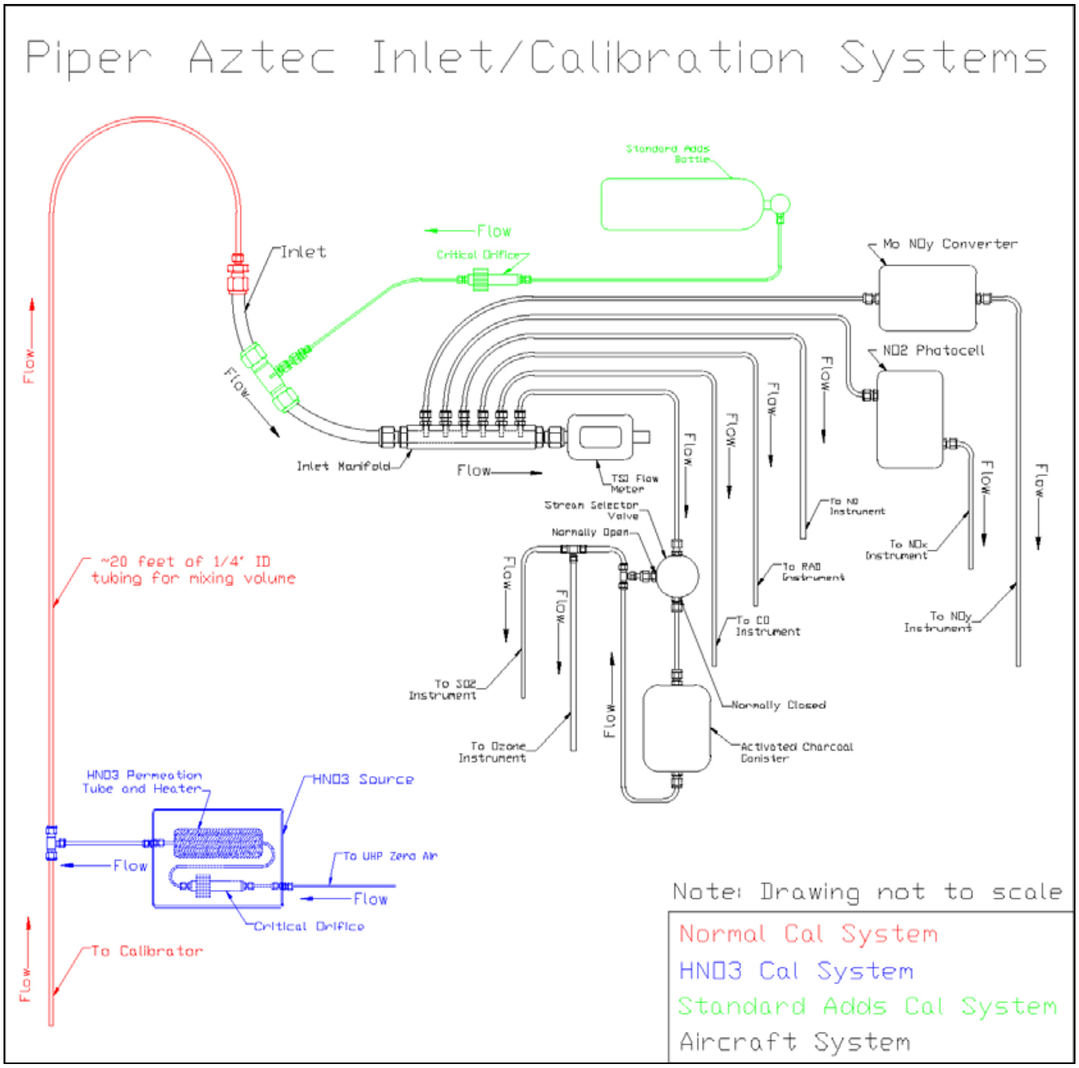



Figure 4-1.  Diagram of Piper Aztec inlet and calibration system.

## $NO_y$ inlet

The $NO_y$ converter used is a standard TEI Mo (molybdenum) converter from a TEI 42C instrument mounted to the rack near the $NO_y$ instrument.  Approximately 8-10 inches of 1/8 inch OD PFA Teflon tubing connects the inlet manifold to the Mo converter.  The 1/8 inch tubing is sleeved into the ¼ inch stainless steel tubing of the Mo converter approximately 2 inches by using a Teflon reducing ferrule.  This minimizes the exposure of the sample to the stainless steel tubing.

## Formaldehyde inlet

The formaldehyde inlet is designed independent of the gas manifold using 1/8 inch PFA Teflon tubing that runs alongside the gas manifold inlet.

### 4.5 CALIBRATION OF SAMPLING EQUIPMENT

The primary method of calibrations will be zero air displacement and dilution of certified high-pressure gas mixtures. These calibrations will be performed before flights and on non-flight days. The pre-flight calibrations will include test atmospheres in addition to the zero determination. Off-day calibrations will focus on ozone response, as well as nitric acid ($HNO_3$) and $NO_2$ $NO_y$ converter efficiencies. In addition, the formaldehyde instrument will be calibrated with a NIST traceable gas standard.

Standard addition calibrations will also be performed during each flight. The main calibration gas cylinder will contain target concentrations of NO at 300 ppmv, $SO_2$ at 300 ppmv, and CO at 1200 ppmv. A secondary gas cylinder will contain $NO_2$ at 300 ppmv. The standard addition calibration level after dilution by the main sample flow is typically 87 ppb.

#### Flight day calibrations

The flight day calibrations will be performed before each science flight. **Table 4-1** lists the levels and time required for each level. The data will be included with each flight or flight series to allow simultaneous processing of the data. These calibrations will be used to ensure continued proper operation of the various instruments.

Table 4-1. Pre-flight calibration levels for the 2006 sampling season.

| **Level** | **Nominal gas concentrations/flows** | **Time (hr:min)** |
|---|---|---|
| 0 | Warm-up of instruments | 3:00 |
| 1 | Zero | 0:10 |
| 2 | 100 ppbv NO/$SO_2$<br>320 ppbv CO | 0:30 |
| 3 | 50 ppbv NO/$SO_2$<br>170 ppbv CO | 0:10 |
| 4 | 100 ppbv Ozone check | 0:10 |
| 5 | 50 ppbv GPT ($NO_2$) | 0:30 |
| 5 | 33 ppbv NO/$SO_2$<br>98 ppbv CO | 0:10 |
| 6 | 20 ppbv NO/$SO_2$<br>60 ppbv CO | 0:10 |
| 7 | 2 ppbv $HNO_3$ 10 SLPM | 0:10 |
| 8 | Zero | 0:10 |
| 9 | ~10 ppbv HCHO | 0:10 |
| 10 | ~20 ppbv HCHO | 0:10 |
| | **Total** (including warm-up) | **5:30** |

**Off-day Calibrations**

The off-day calibrations will be performed on days when a science flight is not planned. Efforts will be made to perform off-day calibrations at regular intervals during the season. The results of the off day calibrations will be used to confirm the response factors obtained from the average of pre-flight calibration results. Off-day calibrations will also be used simply to 'exercise' the instruments during a period of inactivity. **Table 4-2** lists the off-day calibration levels and time required for each level.

As noted, the full calibration will last eight hours and 30 minutes. Due to this significant time requirement, some off-day calibrations will be split between two days, e.g., on the first day, the full ozone calibration will be performed, and on the second day, the multiple NO/$SO_2$/CO levels, gas-phase titrations, formaldehyde, and nitric acid calibrations will be performed.

The data from off-day calibrations will be processed in the same way as the flight data, except that no water, pressure, or response correction factors will be applied. At the end of the field operations, the time series of off-day calibrations will be examined to determine any systematic changes in the response of the various instruments. Systematic changes in instrument response can affect data re-processing. Thus, careful examination of off-day calibrations will be a necessary step to achieve Level 1 data.

Table 4-2. Off-day calibration levels for 2006 sampling season.

| **Level** | **Nominal concentrations/flows** | **Time (hr:min)** |
|---|---|---|
| 0 | Warm-up of instruments | 3:00 |
| 1 | Zero air | 0:10 |
| 2 | $O_3$ 150 ppbv | 0:20 |
| 3 | $O_3$ 125 ppbv | 0:10 |
| 4 | $O_3$ 100 ppbv | 0:10 |
| 5 | $O_3$ 50 ppbv | 0:10 |
| 6 | $O_3$ 25 ppbv | 0:10 |
| | | |
| 1 | Zero air | |
| 2 | NO 150 ppbv[1] | 0:20 |
| 3 | NO 150 ppbv 80% $O_3$ GPT | 0:30 |
| 4 | NO 100 ppbv | 0:10 |
| 5 | NO 100 ppbv 80% $O_3$ GPT | 0:20 |
| 6 | NO 75 ppbv | 0:10 |
| 7 | NO 75 ppbv 80% $O_3$ GPT | 0:20 |
| 8 | NO 30 ppbv | 0:10 |
| 9 | NO 30 ppbv 80% $O_3$ GPT | 0:20 |
| 10 | NO 10 ppbv | 0:10 |
| 11 | NO 10 ppbv 80% $O_3$ GPT | 0:20 |

| Level | Nominal concentrations/flows | Time (hr:min) |
|---|---|---|
| | | |
| 1 | Zero air | 0:10 |
| 2 | $HNO_3$ 10 SLPM | 0:20 |
| 3 | $HNO_3$ 6 SLPM | 0:20 |
| 4 | $HNO_3$ 3 SLPM | 0:20 |
| 5 | $HNO_3$ 1 SLPM | 0:20 |
| | | |
| 1 | Zero air | 0:10 |
| 2 | HCHO 20 ppbv | 0:10 |
| 3 | HCHO 10 ppbv | 0:10 |
| 4 | HCHO 5 ppbv | 0:10 |
| | Total | **9:10** |

Note: The time sequence may vary for each level; indicated time represents maximum time allotted.

**In-flight performance evaluations**

Standard addition calibrations will be performed at least once per flight and will be executed at altitudes above the mixing layer (i.e., planetary boundary layer) or stable clean background air in the mixing layer. The gas mixture will be fed to the manifold as described briefly in **Section 4-4**. The gas mixture that will be used for the standard addition calibration includes NO, $NO_2$, CO, and $SO_2$, propene. The flow rate of the calibration gas will be controlled using a critical orifice and the excess manifold flow will be measured with a TSI flow meter. The expected concentration of the gas in the standard additions is given by:

$$\text{Analyte}_{\text{measured}}\ (\text{ppbv}) = (\text{Analyte}_{\text{cal}}(\text{ppbv}) * \text{Cal flow})/\text{Inlet flow.}$$

## 4.6 AVOIDING CROSS-CONTAMINATION

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

## 4.7 ASSURING REPRESENTATIVE SAMPLES

Flight plans are designed for representative areas of the plume and include constant altitude levels to maintain steady state conditions.

## 4.8 SAMPLE QUANTITIES

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software. Sample quantities will depend on the length of the science flight. Trace gas measurements and $b_{sp}$ are recorded every second, and formaldehyde every 90 seconds.

## 4.9 SAMPLE CONTAINERS

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

## 4.10 SAMPLE IDENTIFICATION

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

## 4.11 SAMPLE PRESERVATION

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software. The electronic media is stored in the computer that collects the data on the aircraft and is backed-up on a CD or flash drive when the aircraft lands.

## 4.12 SAMPLE HOLDING TIME

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software. There is no sample holding time of the sample that is handled by individuals.

## 4.13 SAMPLE SHIPPING

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods or shipping required. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

## 4.14 SAMPLE CHAIN-OF-CUSTODY

**$O_3$, $SO_2$, CO, NO, $NO_2$, $NO_y$, HCHO, and Nephelometer ($b_{sp}$)**

There are no discrete samples handled by individuals for these methods. The identity and disposition of sample measurements are documented electronically by the log associated with the instrument support computer and processing software.

## 4.15 SAMPLE ARCHIVE

Data obtained by Baylor is archived on server and burned to optical drives.

# 5. TESTING AND MEASUREMENT PROTOCOLS

## 5.1 MEASUREMENT METHOD DETAIL

### 5.1.1 Meteorology

Meteorology parameters will be measured with the AIMMS-20 (**A**ircraft **I**ntegrated **M**eteorological **M**easurement **S**ystem). The instrument consists of three distributed measurement modules; an Air Data Module (ADM-20) measuring the physical properties of the flow about the aircraft (barometric pressure, pitot-static pressure for true airspeed, aircraft angle-off-attack, aircraft sideslip, temperature and humidity), a GPS Module (GPS-20) provides position, velocity, carrier-phase and satellite emphemeris data for two GPS antennae located on the aircraft wing tips and an Inertial Measurement Module (IMM-20) providing three-axis accelerations and rates representative of the aircraft motion. The sensor data collected by the individual measurement modules at a basic update rate of 40 Hz is transferred to a high-performance Digital Signal Processing (DSP) module via a high-speed CAN (Controller Area Network) digital serial network bus. The DSP combines the GPS velocity and differential carrier-phase data with the six degree-of-freedom inertial data to precisely define the attitude and velocity of the aircraft at all times to within fractions of one degree and fractions of one meter-per-second respectively. The DSP combines this precise information with fully compensated air-data measurements to compute wind speed with an accuracy of 1/2 knot and wind direction with an accuracy of 5-10 degrees. The processed data is available via a standard RS-232 serial port or the high-speed CAN bus.

### 5.1.2 Altitude and Location

To establish the location represented by each sample collected, measurements of altitude, and global positions are made with an instrument manufactured by Garmin Inc. The Garmin 295 updates altitude and latitude/longitude coordinates at 1 hertz and are recorded by the data system.

### 5.1.3 Ozone

Ozone will be measured with a 2B Technologies Model 205 Dual Beam Ozone Monitor using UV photometry. In the Dual Beam instrument, UV light intensity measurements $I_o$ (ozone-scrubbed air) and I (un-scrubbed air) are made simultaneously, allowing for faster response ~2 seconds.

### 5.1.4 NO, NO, $NO_2$, and $NO_y$

The reactive nitrogen species will be measured using the chemiluminescent reaction with reagent ozone. The chemiluminescence reactions are:

$$NO + O_3 \rightarrow NO_2^*$$

$$\rightarrow NO_2 + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu \ (600 \text{ nm} < \lambda < 2800 \text{ nm})$$

$$NO_2^* + M \rightarrow NO_2 + M$$

$NO_2$* is excited-state $NO_2$ that may emit a red photon upon relaxation (i.e., quenched to the ground state by other species M). During sampling, an ambient sample is mixed with percent levels of ozone at reduced pressure, and the resulting chemiluminescence (*hv*) is measured with a red-filtered photomultiplier tube. In combination with the red filter, this measurement is specific for measurement of nitric oxide (NO).

To measure gas-phase reactive nitrogen species, $NO_y$, (i.e., Σ $NO_2$, $HNO_3$, $N_2O_5$, HONO, peroxyactyl nitrates (PAN), and alkyl nitrates.), a TEI model 42C instrument in conjunction with a Molybdenum (Mo) converter is used.

NO will be measured with a TEI 42C instrument, while $NO_x$ will be measured using an EcoPhysics CLD 77 AM instrument in conjunction with a photolytic converter placed upstream of the chemiluminescence measurement converting $NO_2$ to NO.

### 5.1.5 Sulfur Dioxide

The $SO_2$ measurement is based on the principle that $SO_2$ molecules absorb light between 190 and 230 nm, become excited and decay to a non-excited state. During this transition, the molecules emit ultraviolet light at a different wavelength between 240 and 320 nm that can be detected by a photomultiplier tube. The reaction is as follows:

$$SO_2 + h\nu_1 \rightarrow SO_2^* \rightarrow SO_2 + h\nu_2$$

$$(190 \text{ nm} < h\nu_1 < 230 \text{ nm}; 240 \text{ nm} < h\nu_2 < 320 \text{ nm})$$

The emitted light is proportional to the $SO_2$ concentration. Possible interferences arising from aromatic hydrocarbons is prevented by a hydrocarbon “kicker”. i.e. a wall which discriminates aromatic compounds and $SO_2$ due to their different permeation properties.

### 5.1.6 Carbon Monoxide

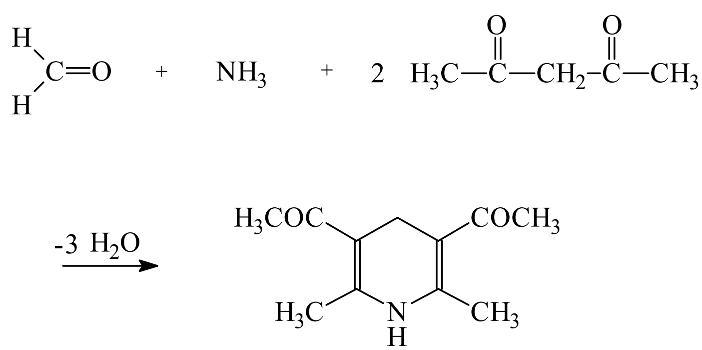
Carbon monoxide will be measured using an Aero Laser vacuum ultraviolet (VUV) fluorescence instrument. This instrument is based on the fluorescence of CO at 150 nm. The fluorescence in the wavelength range between 160 nm and 190 nm is detected by a VUV photomultiplier followed by a fast counter. The VUV light that excites the CO molecules is generated by a lamp that uses an Argon/$CO_2$ gas mixture.

### 5.1.7 Nephelometer

Light scattering ($b_{sp}$) will be measured on the aircraft using nephelometry. In most integrating nephelometers, a white light source is used to illuminate the air sample, and light scattered by particles (and gases) at a particular wavelength is measured using a photomultiplier tube. In the Aztec, a three-wavelength instrument is used (TSI 3563; 450, 550, and 750 nm (blue, green, and red, respectively)). Filters in front of the PMT's are used for wavelength selection. In addition, the TSI instrument provides a separate measurement of particle back-scatter ($b_{scat}$). The instrument automatically calculates Rayleigh scattering from internally measured temperature and pressure and corrects the reported signal for those factors.

### 5.1.8 Formaldehyde

The formaldehyde (HCHO) measurement is based on an aqueous-based reaction with acetylacetone and $NH_3$ to produce α- α'-dimethyl-β- β'-diacetyl-pyridine, which fluoresces at the 510 nm wavelength. The compound is excited by 400 nm light that is generated by a mercury (Hg) lamp. The reaction is as follows:



The instrument measures aqueous formaldehyde, so gaseous formaldehyde is passed over a stripping coil after the flow rates of the solution and the air are measured.

## 5.2 DATA VALIDATION FOR UNPROVEN METHODS

NA

## 5.3 MEASUREMENT SPECIFIC CALIBRATION PROCEDURES

In flight, measurements (i.e., NO, $NO_2$, and $NO_y$) that are based on chemiluminescence will be auto-zeroed every 10 minutes for 30 seconds. These instruments include a modification to allow for matrix zeroing. This is a pre-reaction volume which, combined with appropriate valving, allows mixing the reagent ozone with the sample gas before it reaches the reaction volume. When the zero is activated, the ambient NO (and that NO produced by any upstream converter) is titrated to $NO_2$ before reaching the reaction chamber. Use of this zeroing method allowed for determination of the instrument baseline during operation. In addition, chemiluminescence measurements exhibit some sensitivity to both ambient water and ambient pressure. Both of these dependencies are accounted for in the data processing procedures.

Similarly, CO will be auto-zeroed every 10 minutes for 30 seconds. Because of the water effect on the instrument baseline, a matrix zero is performed on the CO instrument. This will be done by periodically directing the sample gas through palladium on an alumina catalytic converter held at 500°F. In this converter, CO is converted to $CO_2$, but the ambient water vapor is passed quantitatively.

The $SO_2$ and $O_3$ instrument will include a modification to allow for matrix zeroing. This is a modification where the sample volume is diverted with appropriate valving, allowing the sample gas to pass through a cartridge of activated carbon before it reaches the reaction volume. Use of this zeroing method allows for determination of the instrument baseline during operation. The $SO_2$ and $O_3$ zeros are performed automatically once every 30 minutes for 2 minutes.

For the $NO_y$ measurement, the converter is subjected to a $HNO_3$ (nitric acid) conversion efficiency test during the pre-flight and off-day calibrations. The $HNO_3$ calibration gas is generated using a certified permeation tube (Kintek), controlled at 40.0°C and diluted with Scott Marrin ultra-high-purity (UHP) nitrogen. Please see Figure 4-1 for a diagram of this calibration method.

The formaldehyde instrument has a built-in zero that can be activated remotely. Because the sampling period is 90 seconds, the zeros will have to be performed on transit legs

### 5.3.1 Meteorology

The AIMMS-20 system requires a one-time calibration procedure to account for aerodynamic, magnetic and mounting / alignment properties specific to the aircraft type. The calibration procedure consists of a magnetic calibration run performed on the ground followed by a flight calibration run. The details of these calibration procedures are described in this section.

Before starting the magnetic and flight calibration procedures, two physical measurements of the AIMMS-20 installation must be performed. These are the antenna baseline length (distance between the centers of the two GPS antennas mounted on the aircraft wingtips) and the distance between the centerline of the aircraft fuselage and the AIMMS-20 Air Data Probe. The recommended procedure of performing these measurements is to hang a plumb bob from each of the centers of the GPS antennas, the centerline of the Air Data Probe, and the centerline of the fuselage, marking the location of each on the hanger floor. Then a sufficiently long tape measure is used to measure the distance between each of the reference markings noting each for use later in the calibration process.

The magnetic calibration procedure is performed using the standard HyperTerminal software provided with the Microsoft Windows Operating System. Tow or taxi the aircraft in a slow 360 degree circle stopping at the same magnetic heading that you started at. A recommended turning rate is 3 to 6 degrees per second or 1 to 2 minutes for the total maneuver.

The AIMMS-20 Flight Calibration Procedure is described below:

1. Start aircraft, taxi and ascend to an altitude at which you will be insured smooth air with a constant wind field. Depending on the prevailing meteorological conditions this may be well above the temperature inversion and/or cloud top.

2. Select a true air speed (TAS) range representative of your normal aircraft operating procedures and divide this up into 5 speeds. For example, if you normally would fly at 150 knots with a range of 140 to 160 knots select calibration speeds of 140, 145, 150, 155, and 160 knots.

3. Start the calibration procedure by setting up on a true north heading at the lowest airspeed selected in step 3 above.

4. At this lowest airspeed perform a yaw maneuver yawing the aircraft approximately 10 degrees to port followed by ten degrees to starboard, or vice-verse, at a rate of approximately 5 seconds into the yaw and 5 seconds back out for a total of 20 seconds for the complete maneuver.

5. Once the yaw maneuver is complete, hold the lowest airspeed on a constant true north heading for approximately 10 seconds and then increase the airspeed in the increments selected in step 3 above holding each constant for 10 seconds.

6. At the highest TAS repeat the yaw maneuver.

7. Turn the aircraft around 180 degrees and set up on a true south heading at the highest airspeed.

8. Repeat the yaw maneuver.

9. Decrease the airspeed in the steps selected holding each for 10 seconds at a time.

10. Once again perform the yaw maneuver at the lowest TAS setting.

11. Return to base and land.

### 5.3.2 Altitude and Geographical Location

There is not a field calibration for the measurements of altitude and location since the instrument is factory calibrated. Latitude and longitude will be compared against the designated promulgated aerodrome latitude and longitude if available or a designated location at the airport.

### 5.3.3 Ozone

During the pre-flight calibration, the ozone instrument will be challenged with ozone generated by 185 nm photolysis of uncontaminated air within a TEI model 146c gas-phase calibrator. These challenges will be conducted to verify that the instrument is operational and functioning correctly. The data from these challenges will not be used to correct the ozone data on the aircraft, because the ozone output of the calibrator is not known precisely and is not certified as a transfer standard. However, the ozone output of the primary standard that will be used for off-day calibrations is accurate and precise.

During off-day calibrations, the ozone instrument will be calibrated with a TEI model 49C-PS primary ozone standard that is NIST traceable and certified by the EPA (Environmental Protection Agency)

### 5.3.4 NO, $NO_2$, and $NO_y$

The standard pre-flight calibration utilizes both NO and $NO_2$ mixtures to characterize the response of the instruments. The NO mixtures will be made by dilution of a NIST (National Institute of Standards and Technology) traceable high pressure gas mixture (acquired from Scott Marrin Inc.) with zero air using a TEI model 146C gas-phase calibration instrument. The $NO_2$ test gas will be made by gas-phase titration (GPT) of the NO mixture with ozone produced by the calibrator. The NO calibration will be used to establish the basic response factor of the instrument, while the $NO_2$ test gas will be used to determine the $NO_2$ conversion efficiency (CE) of the $NO_x$ and $NO_y$ converters. Further details about the calibration method and levels are provided in **Section 4.5**, but the appropriate equation for the GPT is shown below:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g). \qquad k\ (T=298K) = 1.8 \times 10^{-14}\ cm^3\ mole$$

### 5.3.5 Sulfur Dioxide

The standard pre-flight calibration utilizes $SO_2$ mixtures to characterize the response of the instruments. The $SO_2$ mixtures will be made by dilution of a NIST traceable high pressure gas mixture (acquired from Scott Marrin Inc.) with zero air using a TEI model 146C gas-phase calibration instrument. Further details about the calibration method and levels are provided in **Section 4.5**.

### 5.3.6 Carbon Monoxide

The CO instrument will be calibrated using zero air dilution of a NIST traceable high-pressure gas mixture (acquired from Scott Marrin Inc.). Details about the calibration levels used are presented in **Section 4.5**

### 5.3.7 Light Scattering by Nephelometer

Field calibration of the integrating nephelometer will be performed at least twice during the project. Clean, filtered air and carbon dioxide ($CO_2$) gas, of ultra high purity (UHP) grade, will be used as reference standards. Filtered air will be fed to the instrument before each flight to determine the baseline

### 5.3.8 Formaldehyde

Preflight calibration will be done using a NIST traceable gas cylinder and the TEI Gas Phase Calibrator. In flight performance and calibration will be performed by comparing the reading of the instrument to the known concentration of a standard of additions.

# 6. QA/QC CHECKS

## 6.1 ACCEPTANCE CRITERIA

| Parameter **(units of measure)** | **Method Name or Published Reference** | **Analytical Technique** | **Sample Period (seconds)** | **Detection Limit (units ppb unless otherwise stated)** | **Precision (95% Probability Limits)** | **Accuracy (%Difference unless otherwise stated)** | **Complete-ness *** |
|---|---|---|---|---|---|---|---|
| Ozone - 1 ($O_3$ as ppb) | 40 CFR 58 | UV Photometry | 5 second poll of 10 second updates | 2 | ±15% | ±20% | 80% |
| Sulfur Dioxide ($SO_2$ as ppb) | 40 CFR 58 | Pulsed Fluorescence | 1 second poll of 2 second updates | 1 | ±15% | ±20% | 80% |
| Nitric Oxide (NO as ppb) | 40 CFR 58 | Mo Catalytic Sample Reduction @ 320°C and Chemi-luminescence | 1 second poll of 2 second updates | 2 | ±15% | ±20% | 80% |
| Total Reactive Oxides of Nitrogen ($NO_Y$ as ppb) | 40 CFR 58 | Chemiluminescence | 1 second poll of 2 second updates | 2 | ±15% | ±20% | 80% |
| Nitrogen Dioxide ($NO_2$ as ppb) | N/A | UV Photolysis with Chemiluminescence | 1 second poll of 2 second updates | 1 | ±15% | ±20% | 80% |
| Carbon Monoxide (CO as ppbv) | N/A | Vacuum Ultra Violet (VUV) Fluorescence | 1 second poll of 1 second updates | 2 ($\tau$ = 10s) | ±15% | ±20% | 80% |
| Formaldehyde (HCHO as ppbv) | N/A | Hantsch reaction and fluorescence | 90 | <100 pptv | ±15% | ±20% | 80% |
| Light Scattering (sp and bsp X $10^{-6}$ $m^{-1}$) Red, Green and Blue Wavelengths | N/A | 3 $\lambda$ Nephelometry | 5 | 1x10e$^{-6}$ $m^{-1}$ | ±15% | ±20% | 80% |

| Parameter (units of measure) | Method Name or Published Reference | Analytical Technique | Sample Period | Detection Limit (units ppb unless otherwise stated) | Precision (95% Probability Limits) | Accuracy (%Difference unless otherwise stated) | Complete-ness * |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| **Altitude and Geographical Location** | | | | | | | |
| Altitude (feet above mean sea level) | N/A | Global Positioning System (GPS | 2 | 1 ft | Not specified | ±50 feet | 80% |
| Latitude and Longitude (degrees, minutes, seconds) | N/A | Global Positioning System (GPS) | 2 | 0.04 seconds of Latitude and / or Longitude | Not specified | ±30 seconds of Latitude and / or Longitude | 80% |
| **METEOROLOGICAL PARAMETERS** | | | | | | | |
| Wind Direction (degrees azimuth) | N/A | Inferred from aircraft motion | 1 | 1 Degrees | NA | ±5 degrees azimuth | 80% |
| Wind Speed (knots / meters per second) | N/A | Inferred from aircraft motion | 1 | .1 m/s | NA | ±0.5 m/s | 80% |
| Outside (Ambient) Air Temperature [degrees Celsius ($^o$C)] | N/A | Platinum RTD | 5 | 0.01 Degrees Celsius | NA | ±0.3 degrees C | 80% |
| Pressure [mb] | N/A | Pressure transducer | 1 | 0.01 mb | NA | ±1 mb +0.05% of reading | 80% |
| Relative Humidity (% RH, absolute) | N/A | Solid state sensor | 1 | 0.1% | NA | ±2 % RH | 80% |

## 6.2 PROJECT-SPECIFIC QA OBJECTIVES

QA objectives outlined in this QAPP are commonly used in Atmospheric Sciences and not specific to this project.

## 6.3 ASSESSMENT OF QA OBJECTIVES

The values from the uncertainty analysis will be compared to the QA objective values to determine whether the objectives were met.

## 6.4 OTHER QC CHECKS

General flight tracks have been designed to over-fly as much as possible ground monitoring stations which will allow comparisons to particulate matter, some trace gas measurements, and meteorology.

## 6.5 REQUIRED FREQUENCY AND ACCEPTANCE CRITERIA FOR QC CHECKS

Trace gas measurements will be spanned checked at least once per science flight Preliminary slope factors will be expected to be within 15 % of the most recent previous check.

For aerosol measurements, the response to filtered air will be used and is expected be within 15% before corrective action is performed.

Meteorological measurements will be compared to local conditions before each flight.

# 7. DATA REPORTING, REDUCTION, AND VALIDATION

## 7.1 REPORTING REQUIREMENTS

Units used are listed in the following table:

| | |
|---|---|
| $O_3$, NO, $NO_2$, $NO_y$, $SO_2$, CO, HCHO | ppbv |
| $B_{sp}$, Gsp,Rsp | $Mm^{-1}$ |
| Outside air temperature | deg C |
| Atmospheric Pressure | mb |
| Relative Humidity | % |
| Wind direction | degrees |
| Wind speed | m/s |
| Altitude | feet |
| Latitude | degrees |
| Longitude | degrees |

## 7.2 DELIVERABLES

- Baylor University will deliver time-series plot for gas, aerosol and meteorological data. Additionally, averaged 5 second data files will be delivered.

A final report that summarizes the project and results will be delivered to the HARC.

## 7.3 DATA REDUCTION PROCEDURES

Aircraft Data – Baylor University

### 7.3.1 Reading in Data

The first step in the processing consisted of reading the data, collected using DaqFactory software (Azeotech, Inc.), into Igor. In Igor, a wave was designated for each parameter. The initial waves read into Igor were typically named "A_*parameter*"., where "A" is used to identify data from the Piper Aztec and *parameter* is the name of a measured signal (e.g., ozone). During this step, the latitude/longitude values were interpolated and other waves were formatted. The formatted raw data can be found in the "*parameter*_meas" waves. Also in this step, the autozeros were parsed out of the "measured" data and placed into the "*parameter*_zero" waves. Standard additions data were also parsed out of the "*param*_meas" data and placed into the "*parameter*_SA" waves.

### 7.3.2 Editing Data

Next, the data were manually edited for invalid data points. The macros generated the "*parameter*_meas_edit" and "*parameter*_meas_key" waves from the "*parameter*_meas" waves. During manual editing, data points were removed from the "*parameter*_meas_edit" waves. The "_edit" waves contain the valid data, while the "_key" waves contain valid/invalid flags. The key wave is a numeric value, 0 or 1, that indicates the QC state of the data point. Comments indicating why the points were invalidated were recorded in the notes window.

The data from the "*parameter*_meas_edit" waves were then copied into the "*parameter*_conc" waves. In this step, the autozero values were subtracted from the "measured" data. The baselines for the autozeroed parameters (specifically, Ozone, NO, $NO_2$, $NO_y$, $SO_2$, HCHO, and CO) were therefore adjusted for conditions that affected the instrument background signal, such as instrument temperature, during flight.

The data were adjusted for ground calibration slopes and offsets during the "EnterCalFactors_03()" stage. NO, $NO_2$, and $NO_y$ were all corrected for water interference and pressure effects. The $SO_2$ data was corrected for pressure effects only. The data adjusted in this step was stored in the "*parameter*_calibrated" waves.

The waves were time-shifted to account for different instrument response times. This was a process that was performed by manual inspection, and the time-shifts varied slightly from flight to flight. To shift (but not change) the data, NaN (<u>n</u>ot <u>a</u> <u>n</u>umber) values were inserted or points were deleted at the beginning of the waves so that responses occur simultaneously.

The $NO_2$ concentration was calculated direct NO and $NO_x$ chemiluminescent measurements. The concentration was stored in the "NO2_ppbv_calc" and "NO2_meas_edit" waves.

Although the AIMMS recorded one-second wind direction and wind speed data during flights, Baylor used the AIMMS' one-second north and east wind components (*u* and *v*, respectively) to calculate one-second and five-second averaged wind speed and wind direction data.

First, the one-second component data were edited with all of the other raw waves ("*param*_meas_edit") during the manual editing phase. Then the one-second wind speed and direction data were calculated.

North and east wind components are rectangular coordinates, a simple set of x and y. Wind direction and speed are polar coordinates. Thus, in this step of the processing, the macros converted $u$ (north component) and $v$ (east component) to $r$ (vector length, or wind speed) and $\theta$ (vector direction, or wind direction). This was done via the following equations in Igor:

$$r = \sqrt{u^2 + v^2}$$

$$\theta = \text{Arc tan}(v/u)$$

Because the arc tangent is a function of two numbers, where either or both may be negative but their quotient can be only positive or negative, the vector direction had to be corrected for the specific quadrant (combination of positive/negative $u$ and $v$) by adding a multiple of $\pi$ to $\theta$.

After the one-second wind speed and wind direction data were calculated, the five-second average wind speed and wind direction data were calculated. The same methodology employed above was used to calculate the five-second averaged wind speed and direction data. However, $u$ and $v$ were substituted by five-second scalar averages, $\bar{u}$ and $\bar{v}$, where $\bar{u} = (u_1+u_2+u_3+u_4+u_5)/5$ and $\bar{v} = (v_1+v_2+v_3+v_4+v_5)/5$.

The five-second averaged data were checked for quality and consistency during the EditWindVec() macro. Please see **Table 8-1** for a brief description of each function used in processing. Please see **Figure 7-1** for the sequence of functions.

Table 7-1. Functions used in 2006 Level 0 and Level 1 data processing.

| Function/Macro Name | Purpose |
|---|---|
| *ReadNReduceAztec2003* | Read in binary data, interpolate lat/long, parse out zeros and standard adds |
| *EditAllAztec03* | Sets up graphs for manual editing |
| *CalcConc* | autozeros subtracted from data |
| *EnterCalFactors_06* | ground calibration slopes and offsets applied, as well as other corrections (see **Section 2** for details) |
| *ReduceNO2_03 (Aztec)* | Aztec calculation of $NO_2$ |
| *WindVec* | Creates 1 second wind vectors |
| *AverageWinds* | Averages wind vectors |
| *Generate_AvgData_03* | 1 second data averaged to 5 second data |
| *CheckNOx* | Displays $NO_x$ data for further editing (if necessary) |
| *EditWindVec* | Displays wind data for further editing (if necessary) |
| *WriteQCcodes* | writes QC codes for 5 second data |
| *WriteData_03* | writes data to ASCII tab-delimited text file |

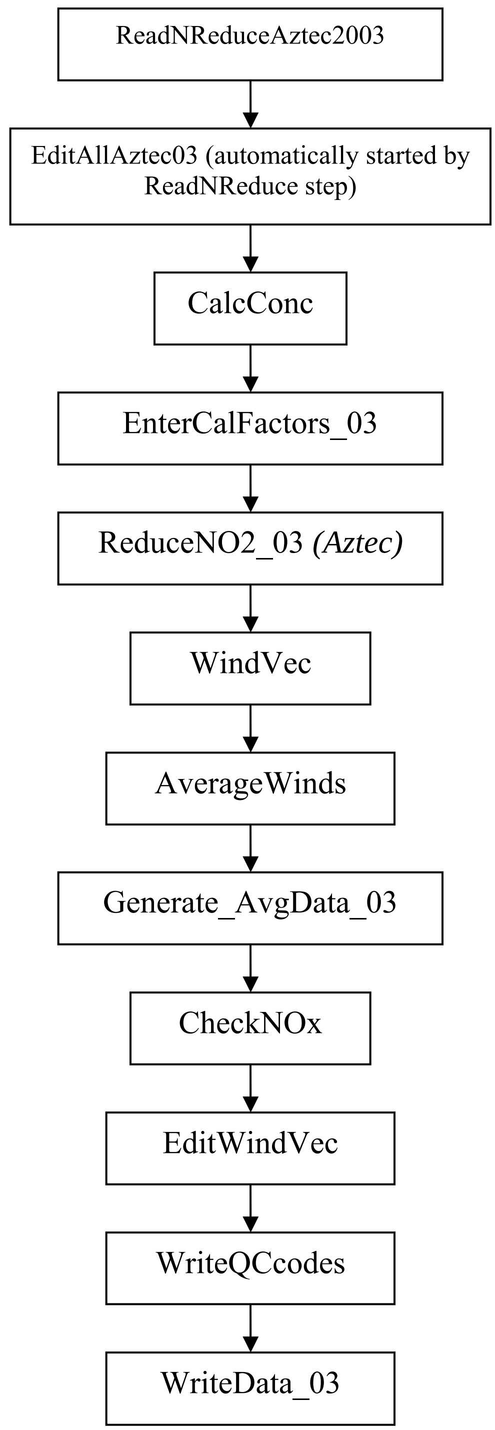



Figure 7-1. Sequence of data processing.

## 7.4 DATA VALIDATION PROCEDURES

Comparisons will be made with ground stations when the aircraft flies near a ground station and the data is available.

## 7.5 DATA STORAGE REQUIREMENTS

Stored on computers for 3 years and backed up to optical media

## 7.6 FINAL DOCUMENTS

The results of this project will be summarized in a joint Final Report and presented in multiple publications in peer reviewed journals.

# 8. ASSESSMENTS

## 8.1 AUDITS

N/A

## 8.2 CORRECTIVE ACTIONS

N/A

## 8.3 PARTIES RESPONSIBLE FOR CORRECTIVE ACTIONS

N/A

# 9. REFERENCES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