Quality Assurance Project Plan

Project 20 – 004

Galveston Offshore Ozone Observations (GO_3)

Prepared for
Texas Air Quality Research Program (AQRP)
The University of Texas at Austin

Prepared by

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Version 5

University of Houston has prepared this QAPP following Environmental Protection Agency (EPA) guidelines for a Quality Assurance (QA) Category III Project: Measurement & Model Application. It is submitted to the Texas Air Quality Research Program (AQRP) as required in the Work Plan requirements.

QAPP Requirements: Project Description and Objectives, Organization and Responsibilities, Scientific Approach, Sampling Procedures, Measurement Procedures, Quality Metrics, Model Selection, Model Calibration, Model Verification, Model Evaluation, Model Documentation, Data Analysis, Interpretation, and Management, Reporting, References

QA Requirements: Technical Systems Audits - Not Required for the Project

Audits of Data Quality – 10% Required

Report of Findings – Required in Final Report

Project Title and Approvals Sheet

This document is a Category III Quality Assurance Project Plan for the *Galveston Offshore Ozone Observations (GO_3) Project*. The Principal Investigator (PI) for the project is James Flynn. Yuxuan Wang, Paul Walter, and Gary Morris are Co-PI's.

Electronic Approvals:

This QAPP was approved electronically on 6/17/2020 by

Vincent M. Torres

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1. PROJECT DESCRIPTION AND OBJECTIVES

1.1. PROCESS AND/OR ENVIRONMENTAL SYSTEM TO BE EVALUATED

This project addresses the 2020-2021 Texas Air Quality Research Program Priority Area of Monitoring Ozone in Galveston Bay and Offshore. The project aims to deploy two small automated sampling systems on commercial boats operating in Galveston Bay (Larry Willis, commercial shrimper) and the offshore waters adjacent to Galveston Island (Ryan Marine Services, crew launch boat operator) to collect routine measurements of O_3 and meteorology, including boundary layer height, during July-October 2020 through a collaboration with the University of Houston (UH) and St. Edward's University (SEU). A third boat, owned and operated by UH, will be utilized for special studies in Galveston Bay as well as for launches of up to 20 ozonesondes to examine vertical profiles of O_3 and confirm ceilometer measurements of boundary layer height. Coupled with 3-D chemical transport modeling, this study will shed light on the conditions and processes that may result in high O_3 over the water and subsequent impacts on the HGB urban area.

1.2. PURPOSE AND OBJECTIVES

Studies have observed high ozone periods in the HGB area driven by large circulation patterns and mesoscale land-sea breeze circulations (Berlin et al., 2013; Caicedo et al., 2019; Langford et al., 2009; Wang et al., 2016). Regional background (non-locally produced) O_3 transported into the area by large-scale winds, is significantly correlated with peak O_3 levels in the HGB region (Berlin et al., 2013; Langford et al., 2009; Nielsen-Gammon et al., 2005). High O_3 events in the HGB were most associated with continental outflow, while the lowest O_3 levels were from onshore winds (Berlin et al., 2013). However, the onshore bay breeze which passes over the industrial regions (e.g. HSC) had significantly elevated regional background O_3 levels than the stronger onshore sea breeze which passes through the Caribbean before entering the Gulf of Mexico (Berlin et al., 2013; Langford et al., 2009). Though episodic, the bay and sea breeze circulation patterns are also found to be important causes for high O_3 events in urban/industrial coastal sites in the U.S. (Banta et al., 2005; Caicedo et al., 2019; Loughner et al., 2011; Mazzuca et al., 2017; Stauffer and Thompson, 2015).

The land/bay/sea breeze phenomenon occurs under weak synoptic forcing when offshore winds sweep urban/industrial pollutants onto open waters, before later reversing as an onshore breeze and bringing the photochemically aged air, which can be high in O_3, back on shore. There is great interest in understanding the O_3 levels in these open waters (i.e. Galveston Bay) which is exposed to a combination of land-based urban and industrial emissions (Wallace et al., 2018), ship emissions (Schulze et al., 2018; Williams et al., 2009), and complex marine O_3 chemistry (i.e. halogen) (Tuite, et al., 2018; Osthoff et al., 2008; Tanaka et al., 2003). Previous studies have observed elevated O_3 levels in these open waters relative to land-based sites (Sullivan et al., 2018; Goldberg et al., 2014). However, unlike land-based measurements, historical records and/or routine measurement of O_3 levels over these waters (i.e. areas where measurement can be difficult) are limited. Available measurements in these regions are generally from ship or airborne measurements during short-intensive sampling campaigns, which were not designed with a focus on O_3 over the water (Mazzuca et al., 2017; Parrish et al., 2009).

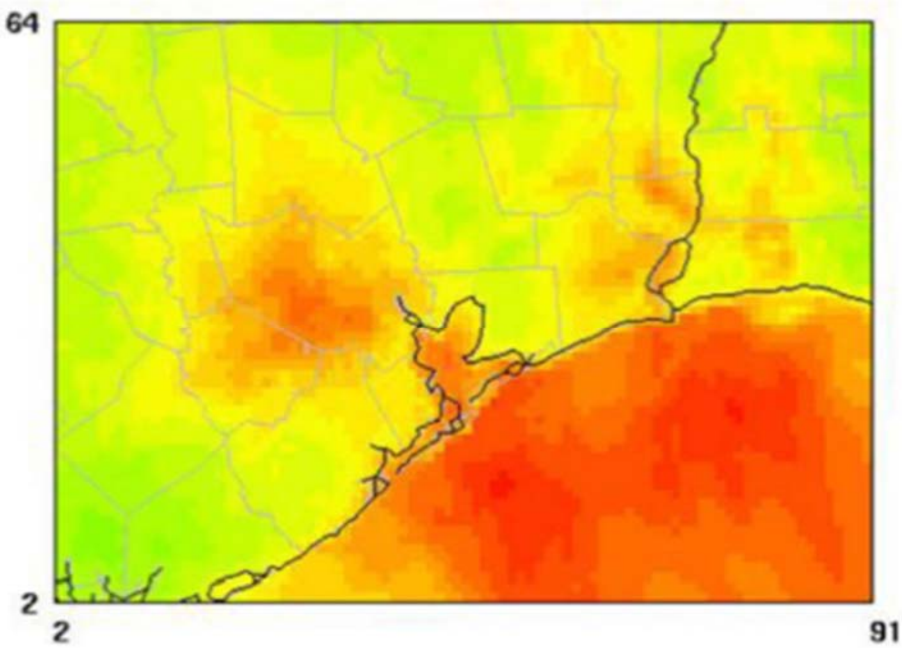
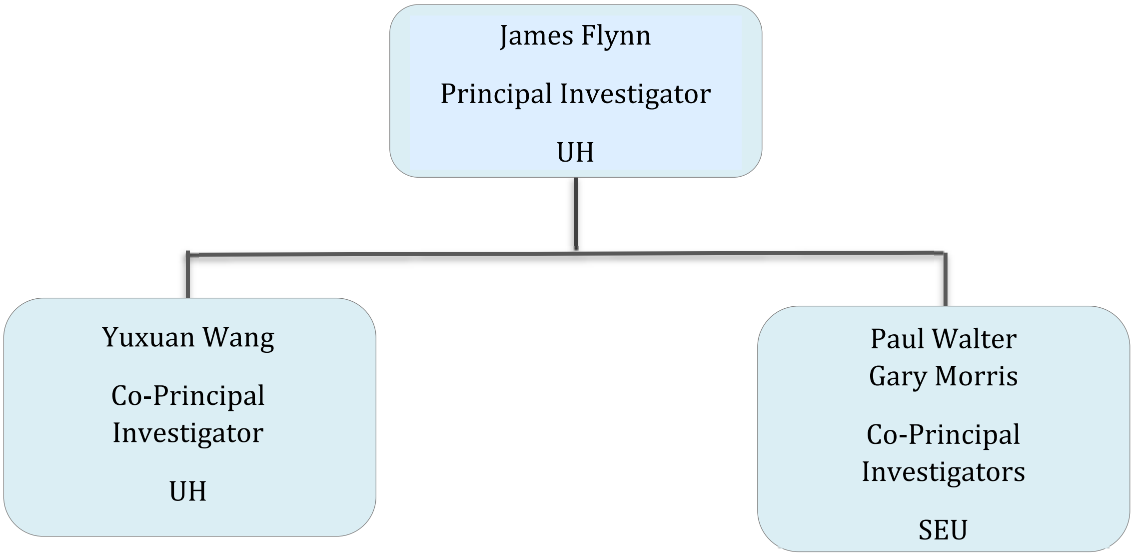


Figure 1. Future case simulation showing high O_3 over water, from Dunker, et al. (2019).

While photochemical models can be powerful tools in detecting and forecasting O_3 levels in these maritime environments (Figure 1), the models are typically built upon parameterizations or simple assumptions to represent small-scale meteorological and chemical processes over the waters. These assumptions/parameterizations need suitable measurements for validation and/or tuning. In addition, current models may not include all important processes, and to identify which processes are missing and their impacts will also require extensive measurements. But routine observations over the waters have been lacking. Due to this, model performance over the marine environments has been largely unconstrained and thus highly uncertain. Previous studies have observed both positive and negative biases of modeled O_3 concentration in these coastal, transitional regions (Caicedo et al., 2019; Dunker et al. 2019; Sullivan et al., 2018; Goldberg et al., 2014; Li et al., 2012; Yerramilli et al., 2012). A recent study of the HGB region and the Galveston Bay compared observation and modeled planetary boundary layer (PBL), wind direction and speed, and O_3 concentrations during a high O_3 event in Houston (Caicedo et al., 2019). They observed a lower correlation between observations and models over bodies of water and coastal regions compared to measurements closer inland (Caicedo et al., 2019). For that study, the discrepancy observed in the coastal and land-water regions was due to a delay in the simulation of onset bay and sea breezes, which are important factors for modeling O_3 (Caicedo et al., 2019). A recent O_3 model study accounted for the changes in local and regional background O_3 levels and found that similar to previous studies, the model performed well for inland sites but overestimated O_3 at the coastal sites, specifically for days with lower O_3 levels (less than 60 ppbv) (Dunker et al., 2019). These model studies incorporated the halogen chemistry proposed by Tuite et al. (2018). However, the chemistry alone was insufficient to match observations, leading the authors to suspect inaccurate emissions in the Gulf of Mexico or incorrect meteorology with respect to the marine boundary layer height and residual layer mixing. Further measurement of O_3 and meteorological conditions directly on Galveston Bay are necessary to understand the high O_3 events in the HGB region and also to improve and refine models.

2. ORGANIZATION AND RESPONSIBILITIES

2.1. KEY PERSONNEL



University of Houston: James Flynn, PI, Department of Earth and Atmospheric Sciences, University of Houston, Houston, Texas, USA, jhflynn@Central.uh.edu. Responsible for overall project management and reporting as well as providing oversight for instrument preparation and deployment. Will coordinate all team efforts as well as interfacing with boat operators and ensuring the UH boat is maintained and operated in a responsible manner.

University of Houston: Yuxuan Wang, Co-PI, Department of Earth and Atmospheric Sciences, University of Houston, Houston, Texas, USA, ywang246@central.uh.edu. Oversight of the modeling and analysis portion of the project, which will be led by a graduate student. Incorporates measurements from the project and supporting sources into model analysis. Assists in project management and reporting.

St. Edward's University: Paul Walter, Co-PI, School of Natural Sciences, St. Edward's University, Austin, Texas, USA, pauljw@stedwards.edu. Responsible for training of UH and SEU personnel for ozonesonde preparation and launch procedures, ozonesonde preparation, launch, and decision making for days to launch, in consultation with project team members. Assists in-person with ozonesonde launches from August 1 – 15, 2020. Will lead SEU portion of the project including reporting to UH and assists in instrument package development and deployment.

St. Edward's University: Gary Morris, Co-PI, School of Natural Sciences, St. Edward's University, Austin, Texas, USA, gmorris1@stedwards.edu. Responsible for obtaining FAA approvals for ozonesonde launches. Assists in-person with ozonesonde launches from August 16 – September 30, 2020. Leads ozonesonde data processing and analysis. Assists with project management and reporting.

2.2. PROJECT SCHEDULE

The project timeline is given below. Note that this schedule does not include the items described in the Deliverables section above as those deliverables will be provided in addition to the performance of the tasks prescribed here. All project participants fully intend to complete all project activities and expend all funds by August 31, 2021. Under the current federal, state, local, and university guidelines in place with respect to COVID-19 we do not anticipate difficulties in successfully completing the project. During the previous "stay-at-home" order the UH field team was designated as essential personnel and allowed to continue operations. Likewise, our commercial operators are commercial operators producing food and providing logistical support to international commerce and are unlikely to be significantly affected as essential operations. All work will be performed in compliance with all federal, state, local, and university safety guidelines. In the event conditions beyond our control change and we are required by federal, state, local, or university guidelines to adjust our operations, the AQRP program manager will be notified immediately.

Task and description	Timeline
Error! Reference source not found. Develop Work Plan	April 27 – May 11, 2020
Error! Reference source not found. Purchase equipment and major components	Within 30 days of receiving AQRP issued start date
Error! Reference source not found. Prepare instrument packages	To begin with Notice to Commence and completed within 30 days of receiving last key component for instrument packages.
Error! Reference source not found. Install instrument packages on commercial vessels and begin collecting data	Within in 14 days of completion of instrument package preparation through October 31, 2020
Error! Reference source not found. R/V Mishepeshu operations	Preparations to begin with AQRP issued start date and be completed by July 31, 2020. Ozonesonde launches to be conducted in August and September 2020.
Error! Reference source not found. Data analysis and modeling	Data analysis to begin as the observational data come in. 3-D modeling setup to begin in August 2020 after the first month's observational data are collected.
Error! Reference source not found. Project reporting and presentation	Continuous from Notice to Commence through October 29, 2021 (Quarterly Report #6). Draft Final Report due August 2, 2021, AQRP presentations in August 2021, Final Report due August 31, 2021. Additional details on specific project reporting can be found in Section **Error! Reference source not found.**.

3. SCIENTIFIC APPROACH

3.1. EXPERIMENTAL DESIGN

The scientific questions to be answered by this work focus on understanding the chemical and physical processes that govern the temporal and spatial patterns of ozone concentrations in the highlighted region. Thus, the measurements and modeling will focus on understanding:

1. How frequently does high ozone reside over the water during the ozone season, and how does the observed frequency compared to that simulated by photochemical models?
2. How does O_3 over water compare with O_3 and O_X ($O_X = O_3 + NO_2$) over adjacent land?
3. How is O_3 formation over the water impacted by local circulation patterns?
4. What are the characteristics of the boundary layer over the water during high O_3 events, and how do the observed boundary layer heights compare to model predicted heights?
5. How do small O_3 and meteorology sampling systems installed on commercial vessels help us better understand O_3 in Galveston Bay and the Gulf of Mexico?

The proposed instrumentation packages will include an O_3 monitor, Global Positioning System (GPS) receiver, all-in-one weather station, and a ruggedized PC with a cellular data connection. The package will operate autonomously when power is available. A ceilometer will be installed on one of the vessels to measure boundary layer height over the water, which is often parameterized in photochemical models and can have a significant impact on model results. The data, which are logged locally, will be sent to servers at UH when within cellular coverage.

The ozonesonde launches will use the electrochemical concentration cell (ECC) type ozonesonde to gather ozone profiles coupled with an InterMet radiosonde to gather meteorological data and with a GPS unit for positional information and wind data. Over the duration of the project, a total of approximately 20 ozonesondes, twice per day (one in the early morning and one in the mid-afternoon) when appropriate meteorological conditions, such as those suggesting enhanced ozone, are forecast.

Modeling activities will utilize the Weather Research and Forecasting (WRF) driven GEOS-Chem (WRF-GC). The model will simulate ozone distributions in the HGB region during the measurement periods with a focus on ozone over the water and land-water ozone gradient. WRF has a powerful and flexible grid system, including multiple nested grids and moving nested grids. For the proposed work, the inner-most model domain of WRF-GC will be set over the sampling areas and adjacent land where the monitoring sites used for comparisons are located at a resolution of 1 kilometer (km) x 1 km, allowing replications of fine-scale temporal and spatial dynamics specific to coastal regions such as sea/bay breeze. In addition to confirming the presence or absence of high O_3 over the water and the conditions that occur during high O_3 events, the results from this project are expected to provide more accurate parameterizations for future modeling studies and to identify partners and methodologies for additional studies.

5.1. MEASUREMENTS PROCESS

In situ O_3 measurements will be performed with a 2B Technology (Boulder, CO) model 205 dual beam O_3 ultraviolet photometric gas analyzers provided by St. Edward's University. A Garmin 19x HVS GPS receiver will provide positional information, and an all-in-one weather station, such as the RM Young Model 92000 weather transmitter will report compass corrected wind speed and direction, temperature, relative humidity, and atmospheric pressure. The Research Vessel (R/V) Mishepeshu, which will be used for launching 20 ECC ozonesondes (En-Sci Corp.), will also be outfitted with the same GPS and weather transmitter for ozonesonde preflight preparations. A Vaisala CL-51 ceilometer will augment one of the instrument packages on one of the boats. If a suitable installation solution is not feasible the ceilometer will be located with the UH sampling site at Smith Point. Each instrument system will be equipped with a ruggedized industrial computer with dual 4G cellular routers to deliver data to the UH servers in near-real time. When out of cellular range, data will continue to be collected and saved locally and will be transmitted back to UH upon returning to adequate cellular coverage.

Data will be collected from these instruments using DAQFactory data acquisition software (Azeotech, Ashland, OR) or Vaisala's BL-View software in the case of the ceilometer. The data will be post-processed and averaged into a format suitable for storage and use in a database with software such as Igor Pro and MATLAB. Ceilometer data may also be processed through the University of Maryland's boundary layer network, which is designed to process data from partner sites into a standard format compliant with EPA reporting requirements.

For ozonesonde launches, pre-launch measurements will include surface pressure, temperature, and humidity for verification of the pre-launch radiosonde observations. If possible, pre-launch ozone concentrations measured by the ECC instrument will be compared with an ozone reading from the R/V Mishepeshu, or from the instrumented commercial boat operating in Galveston Bay. Temperatures should fall within 2˚ Celsius (C), relative humidity (RH) within 10%, and ozone within 10 parts per billion (ppb) before launch occurs. The pump temperature should not exceed 40˚ C at launch. If the pump temperature exceeds 50˚C, the launch will be aborted. The pump current should not exceed 110 milliamps (mA) at launch. If the pump current exceeds 110 mA, the launch will be aborted. The GPS unit should be in contact with at least 5 satellites before launch occurs.

5.2. GENERAL APPROACH

The goals for this project are described by the science questions below:

1. How frequently does high O_3 reside over the water during the O_3 season, and how does the observed frequency compare to that simulated by photochemical models? Under what conditions do the modeled and measured O_3 agree or disagree? Is O_3 consistently elevated over water relative to over land, or is there a spatial variability in O_3 over water?

2. How does O_3 over water compare with O_3 and O_X over adjacent land? Are there indications that O_3 is higher over water due to a lack of titration from point and mobile sources? Are the offshore O_3 values consistent with the findings from previous studies, including the coastal measurements at San Luis Pass in 2016 (Tuite et al., 2018)?

3. How is O_3 formation over the water impacted by local circulation patterns? How does the diurnal pattern over water differ from over land and from coastal measurement locations, such as Smith Point? How frequently does the bay breeze result in a local circulation that brings urban plumes into Galveston Bay? What effect does this circulation have on O_3 in the Houston area in an era of reduced VOC emissions from the Houston Ship Channel area?

4. What are the characteristics of the boundary layer over the water during high O_3 events, and how to the observed boundary layer heights compare to model predicted values? Boundary layer heights over water are often parameterized and may not accurately represent reality, especially in areas with complex land-water interaction and circulation patterns, such as in Galveston Bay and the offshore waters (Dunker et al., 2019). How do the measured boundary layer heights compare to other land-based coastal measurements, such as those from Smith Point during DISCOVER-AQ Houston or from the Galveston 99th St. site (C1034)?

5. How do small O_3 and meteorology sampling systems installed on commercial vessels help us better understand O_3 in Galveston Bay and the Gulf of Mexico? Measurements of O_3 and meteorological parameters have been installed on commercial aircraft, such as in the MOZAIC project (Marenco et al., 1998). Do the vessels operating in Galveston Bay and the offshore coastal areas provide appropriate spatial coverage to investigate O_3 over water under a variety of weather conditions? Can a small sampling system be designed such that it operates with little to no impact on the routine vessel operations?

Sampling will begin as soon as practicable once the instrument systems are ready for deployment. It is possible that due to ordering and shipping times that one or both ozone/met/GPS systems will be completed before the ceilometer arrives. In this case it may be desirable to install the systems onto the boats and install the ceilometer at a later date. The current estimated delivery time of the ceilometer is 3-4 weeks after receiving a purchase order from UH. Final decisions on system deployment schedules will be coordinated with the science and project management teams.

Once deployed the sampling systems will run autonomously and require little to no interaction by the crew. The boat operators will then go about their normal business and sample in the areas shown in Figure 2 below. Individual boats are shown in Figure 3 below.

Figure 2. Map showing routine sampling areas for Larry Willis (red) and the Merchant Vessel (M/V) Red Eagle (green).

Figure 3. Larry Willis' shrimp boat, which operates in Galveston Bay (left), and Ryan Marine's M/V Red Eagle, which operates in the Gulf of Mexico (right).

Figure 4. University of Houston R/V Mishepeshu which will be used for launching ozonesondes in Galveston Bay.

For ozonesonde launches aboard the R/V Mishepeshu (Figure 4) the instruments must be prepared in the lab prior to deployment. Pre-launch instrument conditioning is carried out 3–10 days prior to launch following the procedures recommended by B. Johnson (NOAA, Boulder, CO). Day-of-launch calibration follows the procedures recommended by B. Johnson (NOAA, Boulder, CO) and is summarized in Section 5.1 of the QAPP. Both sets of procedures will be posted on the web (http://ir.stedwards.edu/natural-sciences/ozone) and are summarized in this QAPP. A manual is available on that web site. We note that ozonesonde measurements immediately prior to launch should occur with the instrument elevated 1–2 m above the surface and in the shade.

Larry Willis' shrimping operation averages about 35-40 hours per week on the water catching shrimp in August and September, Tuesday-Sunday, until late October or early November when he switches to oyster season. In speaking with him in June 2020, he does not anticipate the shrimp season closing. Mr. Willis operates in both the food and bait shrimp season and unlike oyster season, has never closed early to the best of his knowledge. In the event of bad weather, he may remain in port on some days, but depending on conditions may be willing to traverse the bays to allow us to collect additional data even if he is not actively shrimping. In the unlikely event that Mr. Willis is unable to support our sampling, the UH R/V Mishepeshu can integrate the measurements from his boat and will be able to operate more extensively in Galveston and Trinity Bays. As a pontoon boat, the R/V Mishepeshu is not suited for operating in the open Gulf of Mexico.

The M/V Red Eagle supports shipping at anchor offshore of the Texas coast, primarily the waters off Galveston Island. The Red Eagle typically makes daily trips into the Gulf of Mexico, however they are an on-call service and the frequency and duration of trips is determined by customer needs.

6. SAMPLING PROCEDURES

All techniques used by the project team members for this project utilize online measurements only. No discrete samples will be collected.

7. MEASUREMENT PROCEDURES

7.1. MEASUREMENT METHODS

Sampling procedures for the ozone instruments will be appropriate for sampling from a boat. All materials are constructed of Teflon. Ambient air is supplied to the ozone monitor through Teflon tubing equipped with in-line filters. The tubing is equipped with an in-line inverted Teflon screen Teflon rain shield and at the end to prevent large particles, bugs, and water from entering the system. The output of the monitor is ASCII text via RS-232C serial connection. The outputs from the instruments are connected to and recorded by data acquisition software on a ruggedized computer every second. Because the ozone and meteorological measurements are in situ techniques, there are no relevant special handling precautions that must be taken.

The ozone measurement is described in detail in Komhyr (1969, 1986). Meteorological measurements made on the payload are described in Thompson et al. (2003, 2007). Accuracy and precision of these measurements is provided in Smit et al. (2007) and Thompson et al. (2019).

Ozonesondes are calibrated using the En-Sci ozonesonde test unit and pump flow meters during the day-of calibration procedure (referenced above and found on our project web site). Intermet iMet radiosondes are calibrated by Intermet, and the calibration data are stored on the radiosonde unit itself. This calibration data is downloaded to the flight computer and interpreted by the flight software. We use SkySonde to process the flight data.

The SkySonde user manual is available at
ftp://ftp.cmdl.noaa.gov/user/emrys/SkySonde%20User%20Manual.pdf.

When discrepancies are found between the GPS altitude and pressure altitude, a pressure offset is implemented and the data are reprocessed (see Morris et al., 2010). Usually these offsets result in <1% changes in troposphere ozone concentrations.

7.2. MEASUREMENT CALIBRATION

Calibration of the ozone monitor will be performed by challenging the instrument with test atmospheres of ozone from an ozone generator what is regularly compared to the EPA region 6's ozone standard reference photometer. This is the same ozone generator that standardizes the ozone monitors as part of UH's HNET monitoring network for the TCEQ. Calibrations of the ozone monitor will be performed in the lab prior to and upon completion of sampling activities, as well as at least once per quarter during the sampling period. Additional checks will be performed after major instrument maintenance is completed if there is a likelihood that the instrument sensitivity has changed. It is anticipated that nominally once per day the instrument baseline will be checked by use of a solenoid valve that will pass the ambient sample through an activated charcoal scrubber to remove ambient ozone. The frequency of background checks will be determined by instrument performance in the sampling environment. Additional calibration and quality assurance (QA) and quality control (QC) checks are described in Section 6.

8. QUALITY METRICS (QA/QC CHECKS)

8.1. QUALITY CONTROL CHECKS

General Information

Comparability is achieved when the results are reported in standard units to facilitate comparisons between the data from this project and other similar programs. In order to accomplish this objective, the reporting units for the ambient monitoring performed here will adhere to standard units (mixing ratios or number densities for gases, per second for photolysis rates, and mass concentration for aerosol composition as a function of size).

The technician assigned to a specific monitoring instrument is responsible for operating samplers and providing minor corrective actions on equipment when required. Equipment problems are generally detected through a failed sample run or through performing routine quality control (QC) checks on a routine basis. The QC checks that are performed on the sampling equipment vary by instrument and are described in the citations referenced previously. When a major equipment problem is involved, the manufacturer is to be contacted, and their responsibility is to follow up on restoring the equipment to its proper operating status. This may be accomplished through telephone consultation with the technician, which may result in the removal of the equipment from the site for repair. Any equipment problems that can result in the loss of data are addressed with a high priority. All situations requiring corrective action will be documented in activity logs. Some specific QC protocols will be discussed following definitions for quality metrics that will be used. An attempt is made to provide adequate information from which to estimate and control the uncertainty and potential limitations of measurements generated by the monitoring. QC activities are generally applied to portions of a measurement process that are both critical to measurement quality and practically subject to evaluation and control. The portions of any given measurement process that are both critical and subject to evaluation and control vary with the measurement being made and the method used. The QC protocol used for any given measurement process may include some or all of the following:

a.) Sampling system contribution to the measurements;

b.) Measurement system contribution to the measurements;

c.) Qualitative performance of the method;

d.) Quantitative performance of the method;

e.) Precision of the measurements; and

f.) Accuracy (bias) of the measurements.

Prior to deployment, the equipment will be powered up, operating parameters will be checked, and the instruments will be tested against various calibration levels. The purpose is to run operational checks to catch problems prior to field deployment, repair all malfunctioning equipment, and familiarize the staff with the equipment. Routine preventive maintenance procedures also are performed continuously during deployment. Routine preventive maintenance procedures and schedules for trace gases measurements are described in individual instrument service manuals. Generally, the PI team, UH staff, and a UH graduate student are responsible for all maintenance of monitoring systems. If problems are observed with particular instruments after being deployed, the manufacturer is to be contacted, and tests are performed to solve the problem. Corrective maintenance procedures also follow the manufacturer's recommendations in the instrument service manuals. To facilitate such procedures, some spare parts are maintained on hand to facilitate rapid repair of common maintenance needs, while others are acquired on an "as needed" basis. Spare parts are receipted, installed according to the manufacturer's instructions, and tested to ensure correct instrument operation.

Data that do not meet acceptance criteria (for any of the instruments used) will have an associated flag attached in electronic files containing the data. In addition, laboratory notebooks will be used by personnel and will be used to specify data flags manually.

Detection limit

Detection limits will be expressed in units of concentration and reflect the smallest concentration of a compound that can be measured with a defined degree of certainty. Criteria pollutants are measured using EPA designated reference or equivalent methods. The detection limits for many of these methods are specified in 40 CFR Part 53. Because of this, no specific measurements of detection limits are made for the criteria pollutants in this project. The analytical instrument detection limit (IDL) for other parameters will be established with the application of available standards according to 40 CFR Part 136, Part B, where applicable.

Blanks/Zeros

The system contribution to the measurement results is determined by analysis of a blank or zero air (filtered air) level as part of each calibration and span check. As part of the calibration, the zero level is used along with the upscale concentrations to establish the calibration curve. As part of the span check, the zero level is used as a quality control check for monitoring zero drift. If a method is found to have a system contribution for a target pollutant at a concentration greater than three times the detection limit or greater than 10 percent of the median measured concentration for the pollutant (whichever is larger), efforts must be taken to remove the contribution. Any system contribution for a target pollutant (or for another constituent that interferes with analysis for a target pollutant) that is above the detection limit must be thoroughly characterized such that the extent of influence on the target pollutant measurement certainty is well understood. This may require an elevated frequency of blank analyses for an adequate period to characterize the contribution. A data flag will be used when concentrations in the blank sample measurements indicate a contribution to the sample measurement result that is determined to be significant relative to the quality objectives specified for the measurement.

Precision

Precision is a measure of the repeatability of the results. Estimates of precision are assessed in different ways for different measurement technologies.

Precision for measurements from continuous monitors will be estimated by analysis of a test atmosphere containing the target compounds being monitored. Precision for trace gases is estimated from precision checks that are done as part of routine span checks of the monitors. This precision check consists of introducing a known concentration of the pollutant into the monitor in the concentration range required by 40 CFR Part 58, Appendix A. The resulting measured concentration is then compared to the known concentration.

Accuracy

Accuracy is the closeness of a measurement to a reference value and reflects elements of both bias and precision. Accuracy will be determined by evaluating measurement system responses for replicate analysis of samples containing the compounds of interest at concentrations representative of the ambient atmospheres typically being monitored during the study as outlined in 40 CFR 58, Appendix A. Note that technical system audits are not required for a Category III QAPP.

Completeness

Data completeness is calculated on the basis of the number of valid samples collected out of the total possible number of measurements. Data completeness is calculated as follows:

% Completeness = (Number of valid measurements x 100)/Total possible number of measurements

Data Auditing

Audits of data quality will be performed by visual inspection of the data (minimum 10% to fulfill Audit of Data Quality requirement), comparison of the data to the QA/QC criteria described in this document, and comparison with other measurements, as applicable. Data that passes these examinations will be deemed acceptable. Should data not pass examination on one or more of the checks, the data will be further examined by the researchers and as appropriate may be flagged as invalid, valid, or valid but having failed a check.

Instrument specifics

Continuous ozone measurements

The UH software will perform automated baseline evaluations (zeros) on a daily basis at a minimum. Instrument data will also be compared to nearby ozone monitors, such as the C1034 for the measurements aboard the M/V Red Eagle and with C1606 for Larry Willis' boat, which typically docks approximately 230 meters west of C1606. Data validity decisions are based only on whether a QC test exceeds the failure limit. Quality Control tasks will consist of calibrations, maintenance, inspections, and record keeping.

Multi-point calibration checks are performed at the beginning and end of sampling and quarterly at a minimum and as needed, such as because of instrument adjustment or repair. Five levels of O_3 calibration gas are introduced into the inlet of the O_3 analyzer by a calibration system. These levels nominally correspond to 200, 100, 75, 50, 25, and 0 parts per billion by volume (ppbv). The O_3 calibration gas is derived from a Thermo 49c-PS O_3 generator that has been standardized with an O_3 SRP by the EPA Region 6 lab in Houston. Single point span and zeros will also be performed at least daily at a minimum to track stability of the instrument.

Ozonesonde measurements

Details of instrument conditioning and calibration can be found in the manuals appearing on the St. Edward's ozonesonde web site described above.

In particular, the following checks are performed as part of the conditioning process:

1. Pump current < 110 mA after running for 10 minutes (min). If not, run longer. If pump current does not decrease below 110 mA, clean pump inlet using methanol (procedure, pull 0.5 cc of methanol through the inlet of the pump 4–5 times). If pump current still does not decrease below 110 mA, return pump to vendor for replacement.

2. Pump pressure > 8 psi after running for 10 min. If not, return to vendor for replacement.

The following checks are performed as part of the day-of flight calibration process:

1. Pump current < 110 mA after running for 10 min. If not within the acceptable range, run longer. If pump current does not decrease below 110 mA, clean pump inlet using methanol (procedure, pull 0.5 cc of methanol through the inlet of the pump 4–5 times). If pump current still does not decrease below 110 mA, return pump to vendor for replacement.

2. Pump response time < 50 s. After running on 5.0 micro amps (μA) level of ozone from ozonizer for 5 min, the ozone is turned off, and the time for the intercell current to drop from 4.0 μA to 1.5 μA is recorded. If not within the acceptable range, replace sonde with another prepped unit and repeat the conditioning process.

3. Pump flow rate > 25 s and < 55 s. With a flow meter connected to the outlet side of the pump, record the time needed for 100 cc of air to flow through the pump. If not within the acceptable range, return to vendor for replacement.

4. Intercell background current < 0.10 µA and > -0.02 µA. After the previous two tests, allow the pump to run on no ozone air for at least 10 min. or until the intercell background current is > -0.02 µA but less than the upper threshold. If not within the acceptable range, replace sonde with another prepped unit and repeat the conditioning process.

The following checks are performed at the launch site:

1. Pump temperature at launch site < 40˚C. If this test fails, punch a hole in the Styrofoam box and turn off pump to allow temperature to cool. Cooling the pump may require the launch team to open the lid of the box and wait 10–15 minutes. If external temperatures are particularly high, the launch team may need to bring the unit into an air-conditioned space to cool. When the pump has cooled, repeat. Pumps with high initial pump currents should not be used on particularly warm days. Running the pump too long before launch on warm days should also be avoided. Every pump should be able to pass this test if it has passed all of the other pre-launch tests. If the launch team cannot launch before the pump temperature reaches 40˚C, they should replace the pump or turn off the pump and wait for it to cool.

2. Ozone reading is compared with the nearest TCEQ surface monitor or 2BTech, as appropriate. Difference should be < 10 ppb. If not, the launch should be delayed until quality of ozonesonde data can be verified.

3. GPS unit has connected to at least 5 satellites for proper tracking.

4. Radiosonde pressure reading is steady and within 5 hPa of surface reading.

The following checks are performed as part of the post-flight calibration process:

1. Compare GPS altitude at burst with pressure altitude at burst. If the difference is > 200 m, reprocess the flight assuming a constant pressure offset.

2. Compare pre-flight surface ozone with the nearest TCEQ surface monitor or 2BTech, as appropriate, to verify sonde was within 10 ppb of surface monitor measurement.

3. For all sondes that reach at least 26 km altitude before burst, compare the column ozone measured by the sonde augmented by the balloon burst climatology of McPeters and Labow

(2012) to yield a total column at the balloon site with Ozone Measuring Instrument (OMI) and other satellite overpass columns or Microtops columns whenever possible. Differences should be < 3%.

4. If either standard #2 or #3 is not met, re-evaluate intercell background current data and adjust, if necessary, to match the calibration data.

4.1. QUALITY ASSURANCE OBJECTIVES

There are no additional QA objectives beyond those described previously for the continuous measurements.

An example of the ozonesonde pre-flight checklists are in Appendix A and can be found on the website at:

http://ir.stedwards.edu/natural-sciences/ozone

These checklists highlight the range of checks each instrument undergoes and the acceptable range of critical measurements before an instrument is cleared for flight.

5. MODEL SELECTION

The key objective of the modeling aspect of this project is to interpret the data collected to answer the science questions. To achieve this objective, it is required to use a 3-D chemical transport model with fine resolutions that can resolve the Galveston Bay. Thus, we select 3-D chemical transport model, Weather Research and Forecasting (WRF) - driven GEOS-Chem (WRF-GC) (Lin et al., 2020). WRF has a powerful and flexible grid system, including multiple nested grids and moving nested grids. For the proposed work, the inner-most model domain of WRF-GC will be set over the sampling areas (i.e. the Galveston Bay and Gulf of Mexico portion shown in Figure 2) at a resolution of 1 km x 1 km. The advantage of fine-resolution meteorology that comes with WRF will allow replications of fine-scale temporal and spatial dynamics specific to coastal regions such as sea/bay breeze. The GEOS-Chem model has a state-of-the-science, well-documented, and benchmarked chemical module that fully couples gaseous and aerosol chemistry, including the recent development of halogen chemistry, which is of particular utility for coastal environments. Combining the advantages of the two models, WRF-GC will allow us to simulate the chemical and dynamical complexity of the proposed field measurements.

6. MODEL CALIBRATION

The GEOS-Chem chemical transport model has a standard benchmarking procedure for each major code release, using observations compiled from surface monitoring network, aircraft campaigns, and satellite retrievals around the globe. During the benchmarking procedure, each module of the model, including transport, emission, chemistry, dry deposition, and wet deposition, is calibrated and best parameters are chosen based on the benchmarking results. For example, observed global distribution of radon is used to calibrate the transport process. This project will use the most recent public release to date (on the date of project initiation), which has gone through the benchmarking procedure.

7. MODEL VERIFICATION

The objective of model verification is to use existing observations to verify the model's ability to simulate the overall features of meteorology, ozone and its precursors, during the study period. We will verify the model by comparing the simulation results with surface observations (e.g. TCEQ CAMS data of MDA8 ozone) in Houston. These data are independent from the field campaign observations to be collected and are publicly available. The model verification uses the same metrics described in the Model Evaluation section (Table 2).

8. MODEL EVALUATION

The model will be evaluated by comparing the model prediction of meteorology, ozone and ozone precursors with observational data collected from the field campaign. The model evaluation will use the performance metrics listed in Table 2. These particular metrics were selected because they are among the most commonly used standard statistical metrics to evaluate the simulated variability (e.g. correlation coefficient) and magnitudes in both absolute mean bias (MB) and mean absolute error (MAE) and relative terms normalized mean bias (NMB). The root mean square error (RMSE) gives more weights to model errors with larger absolute values than MAE, making it more appropriate to evaluate the model's ability to simulate high ozone cases over the Galveston Bay.

The metrics of model evaluation will be compared with published results of GEOS-Chem ozone simulation (e.g. Zhang et al., 2011). To audit modeling results (10% required), we will invite a few members from the GEOS-Chem development team and users' community to review at least 10% of the modeling results, which will be selected randomly from the outputs, to satisfy the Audit of Data Quality requirement; potential peer reviewers are Dr. Daniel Jacob at Harvard University and Dr. Lin Zhang at Peking University.

Table 2. Performance metrics of model evaluation.

Mean Bias (MB)	$MB = 1/N\sum_{i=1}^{N}(M_i - O_i)$
Mean Absolute Error (MAE)	$MAE = 1/N\sum_{i=1}^{N}\lvert M_i - O_i \rvert$
Normalized Mean Bias (NMB)	$NMB = \frac{\sum_{i=1}^{N}(M_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100\%$
Correlation Coefficient (Corr. R)	$Corr.R = \frac{\sum_{i=1}^{N}(M_i - \overline{M})(O_i - \overline{O})}{\sqrt{\sum_{i=1}^{N}(M_i - \overline{M})^2}\sqrt{\sum_{i=1}^{N}(O_i - \overline{O})^2}}$
Root Mean Square Error (RMSE)	$RMSE = \sqrt{1/N\sum_{i=1}^{N}(M_i - O_i)^2}$

Note: M is the model output, O is the observation, N is the number of samples, and $\overline{M} = 1/N\sum_{i=1}^{N} M_i$, $\overline{\mathrm{O}} = 1/N\sum_{i=1}^{N} O_i$.

9. MODEL DOCUMENTATION

We will maintain documentation files for each model run that identifies model code versions, dates, analyses, and input and output files. Each input/output file used will be reviewed for quality assurance purposes using various visualization methods, including software animations and graphing, as well by quantitative filtering using selected filter criteria to identify anomalous data. The model documentation will include summaries of the input file values that were changed, the boundary conditions, and why the changes were made; the analysis of the output files, and any other important instructions required to replicate each run.

10. DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT

10.1. DATA REPORTING REQUIREMENTS

The data will be provided in time-stamped delimited text format, likely in 1- or 5-minute averages or other suitable formats as appropriate in order for the data to be used by subsequent users, such as the AQRP or TCEQ. Data will include the time series (and relevant GPS information) of all parameters discussed above. Ozonesonde data will consist of delimited text files for each flight as well as standard plots of vertical profiles.

The output of much of the instrumentation to be used consists of time series of the measured parameters; these time series will undergo quality assurance procedures that are described in this QAPP. These time series will be utilized in standard statistical analyses (average, median, standard deviation, etc.) as well as in the determination of diurnal profiles, probability density as a function of wind direction, etc. In addition to wind direction probabilities, backward trajectory clustering will provide a first-pass at larger scale transport pathways.

All ozonesonde data are processed using the SkySonde software of A. Jordan. The key equation used to calculate ozone concentrations from the intercell current measurement is:

$$ppO_3 = C \times T_{pump} \times t_{100} \times \gamma \times (I_{cell} - I_{background})$$

where ppO_3 is the partial pressure of O_3 in mPa, C is a constant = 4.309×10^{-4}, T_{pump} is the pump temperature in K, t_{100} is the time required for the pump to process 100 cc of air, γ is the pressure dependent correction for pump efficiency (empirically determined or recommended by pump manufacturer), I_{cell} is the intracell current, and $I_{background}$ is the pre-flight, zero-ozone background current.

We also will use a multi-scale modeling framework that uses the Weather Research and Forecasting (WRF) meteorology model to drive the GEOS-Chem chemical transport model, named WRF-GC (Lin et al., 2020). This modeling framework is a new capability of the GEOS-Chem chemical transport model, which has been successfully applied by the project team to interpret SAFS 2017 field measurement data and simulate long-range transport of fire emissions from Central America to Corpus Christi and Houston (Wang et al., 2018). WRF has a powerful and flexible grid system, including multiple nested grids and moving nested grids. The advantage of fine-resolution meteorology that comes with WRF will allow replications of finescale temporal and spatial dynamics specific to coastal regions such as a sea/bay breeze. The GEOS-Chem model has a state-of-the-science, well-documented, and benchmarked chemical module that fully couples gaseous and aerosol chemistry, including the recent development of halogen chemistry, which is of particular utility for coastal environments. Combining the advantages of the two models, WRF-GC will allow us to simulate the chemical and dynamical complexity of the proposed field measurements.

10.2. DATA VALIDATION PROCEDURES

Ambient data that have passed the QA/QC checks described in Section 6 above will be considered to be validated. Additional comparisons to external measurements as appropriate will be completed and reported as part of the data analysis and subsequent reporting to the AQRP.

For ozonesonde measurements pre-flight surface ozone readings at the launch site are compared with concurrent readings from the nearest ozone monitor, as appropriate. Post-flight, ozone columns generated by the sonde instruments are compared (where possible) with column retrievals from the Ozone Monitoring Instrument (OMI; www.nasa.gov/mission_pages/aura/spacecraft/omi.html) overpasses. Further, the radiosonde’s pressure altitude is compared with its GPS altitude. These data validation checks are performed for every flight. For the required 10% audit for data quality for Category III projects, we will perform visual inspection and compare at least 10% of the GO_3 ozonesonde profiles for altitudes > 5 km AMSL to the seasonal averages of past flights from the Houston area.

10.3. DATA ANALYSIS

Data analysis will include statistical and correlation as well as an assessment of spatial and diurnal trends. Geospatial tools will be used to assess whether certain areas exhibit consistent patterns of high ozone or large variability. Data will also be separated by area, such as within Galveston Bay or in the Gulf of Mexico, over open water or near shore, and proximity to shipping lanes. Meteorological conditions will also be considered when analyzing this data set. Back trajectories will be used to determine the source and of the air mass with open water, land, or areas of known or suspected emissions. Data will be binned by days dominated by local circulation and days dominated by synoptic flows, as well as photochemically active vs. low O_3 days. Ozonesonde analysis will use same-day morning and afternoon launches to examine how residual layer ozone correlates with the boundary layer ozone for select days in Galveston Bay, with a focus on high ozone episodes. Our expectation is that the morning/afternoon profile comparison in Galveston Bay will be rather different than what is often observed from inland locations.

Additional sources of data will likely include analysis of winds aloft from the radar wind profiler and boundary layer heights at La Porte (Questions 3, 4). Trace gases such as O_3 and NO_X from land-based sites including Smith Point (C1606), Seabrook Friendship Park (C45), and La Porte Sylvan Beach (C556, O_3 only), and Galveston 99th St. (C1034) will be used to assess the relative difference between O_3 over the bay and coastal waters and whether the differences observed between measurements on water and land may be due to titration from NO_X emissions (Questions 1, 2).

An assessment of the suitability for installing small sampling packages aboard commercial vessels will also be provided. This assessment will consider the area of operations, access, cost, utility of the data generated, and specific challenges that were encountered as a result of the sampling approach (Question 5). This assessment will help guide future experiments that may take place in Galveston Bay, the Gulf of Mexico, or other coastal areas that may experience similar conditions. Suggestions for potential improvements and/or changes in operations will also be included.

All the observational data collected (chemical and meteorological) will be compared to the corresponding outputs from a 3-D chemical transport model, Weather Research and Forecasting (WRF) - driven GEOS-Chem (WRF-GC) (Lin et al., 2020). The model will simulate ozone distributions in the HGB region during the measurement periods with a focus on ozone over the water and land-water ozone gradient. WRF has a powerful and flexible grid system, including multiple nested grids and moving nested grids. For the proposed work, the inner-most model domain of WRF-GC will be set over the sampling areas (i.e. the Galveston Bay and Gulf of Mexico portion shown in Figure 2. Map showing routine sampling areas for Larry Willis (red) and the Merchant Vessel (M/V) Red Eagle (green). at a resolution of 1 km x 1 km. The advantage of fine-resolution meteorology that comes with WRF will allow replications of fine-scale temporal and spatial dynamics specific to coastal regions such as sea/bay breeze. The GEOS-Chem model has a state-of-the-science, well-documented, and benchmarked chemical module that fully couples gaseous and aerosol chemistry, including the recent development of halogen chemistry, which is of particular utility for coastal environments. Combining the advantages of the two models, WRF-GC will allow us to simulate the chemical and dynamical complexity of the proposed field measurements.

The WRF-GC modeling analysis will address Questions 1-4. Specifically, we will analyze the spatiotemporal consistency (or inconsistency) between simulated and observed ozone patterns and high ozone events over Galveston Bay and GOM (Question 1) and between simulated and observed boundary layer heights and other meteorological parameters such as winds (Question 3). The model-to-observation differences will be binned by sampling locations (over waters vs. on the coast), weather conditions (e.g. high vs. low temperature), circulation patterns (sea breeze days vs. synoptic flow days), NO_X levels, and other factors that will emerge from the analysis. These composite comparisons will reveal possible drivers of model biases and help answer Questions 2 and 3.

After we have a good understanding of model performance and biases under different conditions, we will select different ozone cases (e.g., high ozone over water and high ozone over land) to better identify and attribute the gaps within the models that need to be improved. The focus of this analysis will be on ozonesonde measurements that capture the vertical structure of coastal environments (over land and over water). We will add tagged tracers in the model to represent different air masses and conduct perturbation simulations to probe the impact of different processes (or key parameters for a given process) on model performance such as but not limited to PBL height, ozone deposition over water, halogen chemistry, and shipping emissions.

10.4. DATA STORAGE

Data collected/generated during the course of this project will be backed up on each institution's servers, or at UH and backed up on a UH owned backup server at Rice University to provide "cold storage" for the UH server at an off-site location and will be maintained for a minimum of 3 years after the completion of the project. The choice of Rice University as the off-site server location was based on a record of long-term and extensive collaboration between the two schools.

11. REPORTING

AQRP requires certain reports to be submitted on a timely basis and at regular intervals. A description of the specific reports to be submitted and their due dates are outlined below. One report per project will be submitted (collaborators will not submit separate reports), with the exception of the Financial Status Reports (FSRs). The lead PI will submit the reports, unless that responsibility is otherwise delegated with the approval of the AQRP Project Manager. All reports will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. Report templates and accessibility guidelines found on the AQRP website at http://aqrp.ceer.utexas.edu/ will be followed.

Abstract: At the beginning of the project, an Abstract will be submitted to the AQRP Project Manager for use on the AQRP website. The Abstract will provide a brief description of the planned project activities and will be written for a non-technical audience.

Abstract Due Date: Friday, July 31, 2020

Quarterly Reports: Each Quarterly Report will provide a summary of the project status for each reporting period. It will be submitted to the AQRP Project Manager as a Microsoft Word file. It will not exceed 2 pages and will be text only. No cover page is required. This document will be inserted into an AQRP compiled report to the TCEQ.

Quarterly Report Due Dates:

Report	Period Covered	Due Date
Quarterly Report #1	May, June, July 2020	Friday, July 31, 2020
Quarterly Report #2	August, September, October 2020	Friday, October 30, 2020
Quarterly Report #3	November, December 2020, January 2021	Friday, January 29, 2021
Quarterly Report #4	February, March, April 2021	Friday, April 30, 2021
Quarterly Report #5	May, June, July 2021	Friday, July 30, 2021
Quarterly Report #6	August, September, October 2021	Friday, October 29, 2021

Monthly Technical Reports (MTRs): Technical Reports will be submitted monthly to the AQRP Project Manager and TCEQ Liaison in Microsoft Word format using the AQRP FY20-21 MTR Template found on the AQRP website.

MTR Due Dates:

Report	Period Covered	Due Date
Technical Report #1	Project Start - June 30, 2020	Friday, July 10, 2020
Technical Report #2	July 1 - 31, 2020	Monday, August 10, 2020
Technical Report #3	August 1 - 31, 2020	Thursday, September 10, 2020
Technical Report #4	September 1 - 30 2020	Friday, October 9, 2020
Technical Report #5	October 1 - 31, 2020	Tuesday, November 10, 2020
Technical Report #6	November 1 - 30, 2020	Thursday, December 10, 2020
Technical Report #7	December 1 - 31, 2020	Friday, January 8, 2021
Technical Report #8	January 1 - 31, 2021	Wednesday, February 10, 2021
Technical Report #9	February 1 - 28, 2021	Wednesday, March 10, 2021
Technical Report #10	March 1 - 31, 2021	Friday, April 9, 2021
Technical Report #11	April 1 - 30, 2021	Monday, May 10, 2021
Technical Report #12	May 1 - 31, 2021	Thursday, June 10, 2021
Technical Report #13	June 1 - 30, 2021	Friday, July 9, 2021
Technical Report #14	July 1 - 31, 2021	Tuesday, August 10, 2021

DUE TO PROJECT MANAGER

Financial Status Reports (FSRs): Financial Status Reports will be submitted monthly to the AQRP Grant Manager (RoseAnna Goewey) by each institution on the project using the AQRP 20-21 FSR Template found on the AQRP website.

FSR Due Dates:

Report	Period Covered	Due Date
FSR #1	Project Start - June 30, 2020	Wednesday, July 15, 2020
FSR #2	July 1 - 31, 2020	Friday, August 14, 2020
FSR #3	August 1 - 31, 2020	Tuesday, September 15, 2020
FSR #4	September 1 - 30 2020	Thursday, October 15, 2020
FSR #5	October 1 - 31, 2020	Friday, November 13, 2020
FSR #6	November 1 - 31, 2020	Tuesday, December 15, 2020
FSR #7	December 1 - 31, 2020	Friday, January 15, 2021
FSR #8	January 1 - 31, 2021	Monday, February 15, 2021
FSR #9	February 1 - 28, 2021	Monday, March 15, 2021
FSR #10	March 1 - 31, 2021	Thursday, April 15, 2021
FSR #11	April 1 - 30, 2021	Friday, May 14, 2021
FSR #12	May 1 - 31, 2021	Tuesday, June 15, 2021
FSR #13	June 1 - 30, 2021	Thursday, July 15, 2021
FSR #14	July 1 - 31, 2021	Friday, August 13, 2021
FSR #15	August 1 - 31, 2021	Wednesday, September 14, 2021
FSR #16	Final FSR	Friday, October 15, 2021

DUE TO GRANT MANAGER

Draft Final Report: A Draft Final Report will be submitted to the AQRP Project Manager and the TCEQ Liaison. It will include an Executive Summary. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources. It will also include a report of the QA findings.

Draft Final Report Due Date: Monday, August 2, 2021

Final Report: A Final Report incorporating comments from the AQRP and TCEQ review of the Draft Final Report will be submitted to the AQRP Project Manager and the TCEQ Liaison. It will be written in third person and will follow the State of Texas accessibility requirements as set forth by the Texas State Department of Information Resources.

Final Report Due Date: Tuesday, August 31, 2021

Project Data: All project data including but not limited to QA/QC measurement data, metadata, databases, modeling inputs and outputs, etc., will be submitted to the AQRP Project Manager within 30 days of project completion (September 20, 2021). The data will be submitted in a format that will allow AQRP or TCEQ or other outside parties to utilize the information. It will also include a report of the QA findings.

AQRP Workshop: A representative from the project will present at the AQRP Workshop in the first half of August 2021.

Presentations and Publications/Posters: All data and other information developed under this project which is included in **published papers, symposia, presentations, press releases, websites and/or other publications** shall be submitted to the AQRP Project Manager and the TCEQ Liaison per the Publication/Publicity Guidelines included in Attachment G of the Subaward.

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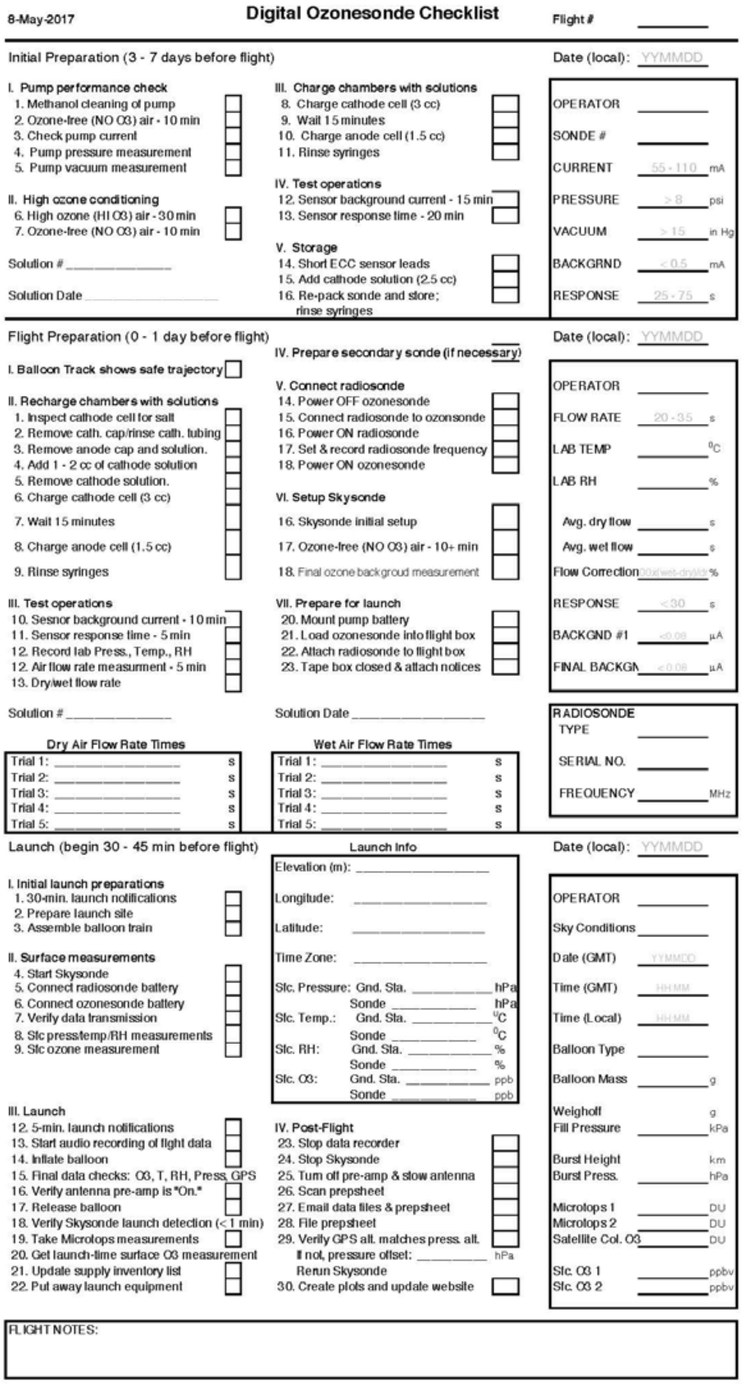
Appendix A – Ozonesonde preparation sheet



8-May-2017

Digital Ozonesonde Checklist

Flight # ________

Initial Preparation (3 - 7 days before flight)

Date (local): YYMMDD

I. Pump performance check
1. Methanol cleaning of pump ☐
2. Ozone-free (NO O3) air - 10 min ☐
3. Check pump current ☐
4. Pump pressure measurement ☐
5. Pump vacuum measurement ☐

II. High ozone conditioning
6. High ozone (HI O3) air - 30 min ☐
7. Ozone-free (NO O3) air - 10 min ☐

Solution # ______________

Solution Date ____________________

III. Charge chambers with solutions
8. Charge cathode cell (3 cc) ☐
9. Wait 15 minutes ☐
10. Charge anode cell (1.5 cc) ☐
11. Rinse syringes ☐

IV. Test operations
12. Sensor background current - 15 min ☐
13. Sensor response time - 20 min ☐

V. Storage
14. Short ECC sensor leads ☐
15. Add cathode solution (2.5 cc) ☐
16. Re-pack sonde and store; rinse syringes ☐

OPERATOR ________
SONDE # ________
CURRENT 55 - 110 mA
PRESSURE > 8 psi
VACUUM > 15 in Hg
BACKGRND < 0.5 mA
RESPONSE 25 - 75 s

Flight Preparation (0 - 1 day before flight)

Date (local): YYMMDD

I. Balloon Track shows safe trajectory ☐

II. Recharge chambers with solutions
1. Inspect cathode cell for salt ☐
2. Remove cath. cap/rinse cath. tubing ☐
3. Remove anode cap and solution. ☐
4. Add 1 - 2 cc of cathode solution ☐
5. Remove cathode solution. ☐
6. Charge cathode cell (3 cc) ☐
7. Wait 15 minutes ☐
8. Charge anode cell (1.5 cc) ☐
9. Rinse syringes ☐

III. Test operations
10. Sesnor background current - 10 min ☐
11. Sensor response time - 5 min ☐
12. Record lab Press., Temp., RH ☐
12. Air flow rate measurment - 5 min ☐
13. Dry/wet flow rate ☐

Solution # ______________

IV. Prepare secondary sonde (if necessary) ____

V. Connect radiosonde
14. Power OFF ozonesonde ☐
15. Connect radiosonde to ozonsonde ☐
16. Power ON radiosonde ☐
17. Set & record radiosonde frequency ☐
18. Power ON ozonesonde ☐

VI. Setup Skysonde
16. Skysonde initial setup ☐
17. Ozone-free (NO O3) air - 10+ min ☐
18. Final ozone backgroud measurement ☐

VII. Prepare for launch
20. Mount pump battery ☐
21. Load ozonesonde into flight box ☐
22. Attach radiosonde to flight box ☐
23. Tape box closed & attach notices ☐

Solution Date __________________

OPERATOR ________
FLOW RATE 20 - 35 s
LAB TEMP ________ ^{0}C
LAB RH ________ %
Avg. dry flow ________ s
Avg. wet flow ________ s
Flow Correction 00x(wet-dry)/dr %
RESPONSE < 30 s
BACKGND #1 <0.08 µA
FINAL BACKGN < 0.08 µA

RADIOSONDE
TYPE ________
SERIAL NO. ________
FREQUENCY ________ MHz

Dry Air Flow Rate Times

Trial 1: ________________ s
Trial 2: ________________ s
Trial 3: ________________ s
Trial 4: ________________ s
Trial 5: ________________ s

Wet Air Flow Rate Times

Trial 1: ________________ s
Trial 2: ________________ s
Trial 3: ________________ s
Trial 4: ________________ s
Trial 5: ________________ s

Launch (begin 30 - 45 min before flight)

Date (local): YYMMDD

I. Initial launch preparations
1. 30-min. launch notifications ☐
2. Prepare launch site ☐
3. Assemble balloon train ☐

II. Surface measurements
4. Start Skysonde ☐
5. Connect radiosonde battery ☐
6. Connect ozonesonde battery ☐
7. Verify data transmission ☐
8. Sfc press/temp/RH measurements ☐
9. Sfc ozone measurement ☐

III. Launch
12. 5-min. launch notifications ☐
13. Start audio recording of flight data ☐
14. Inflate balloon ☐
15. Final data checks: O3, T, RH, Press, GPS
16. Verify antenna pre-amp is "On." ☐
17. Release balloon ☐
18. Verify Skysonde launch detection (< 1 min)
19. Take Microtops measurements ☐
20. Get launch-time surface O3 measurement
21. Update supply inventory list ☐
22. Put away launch equipment ☐

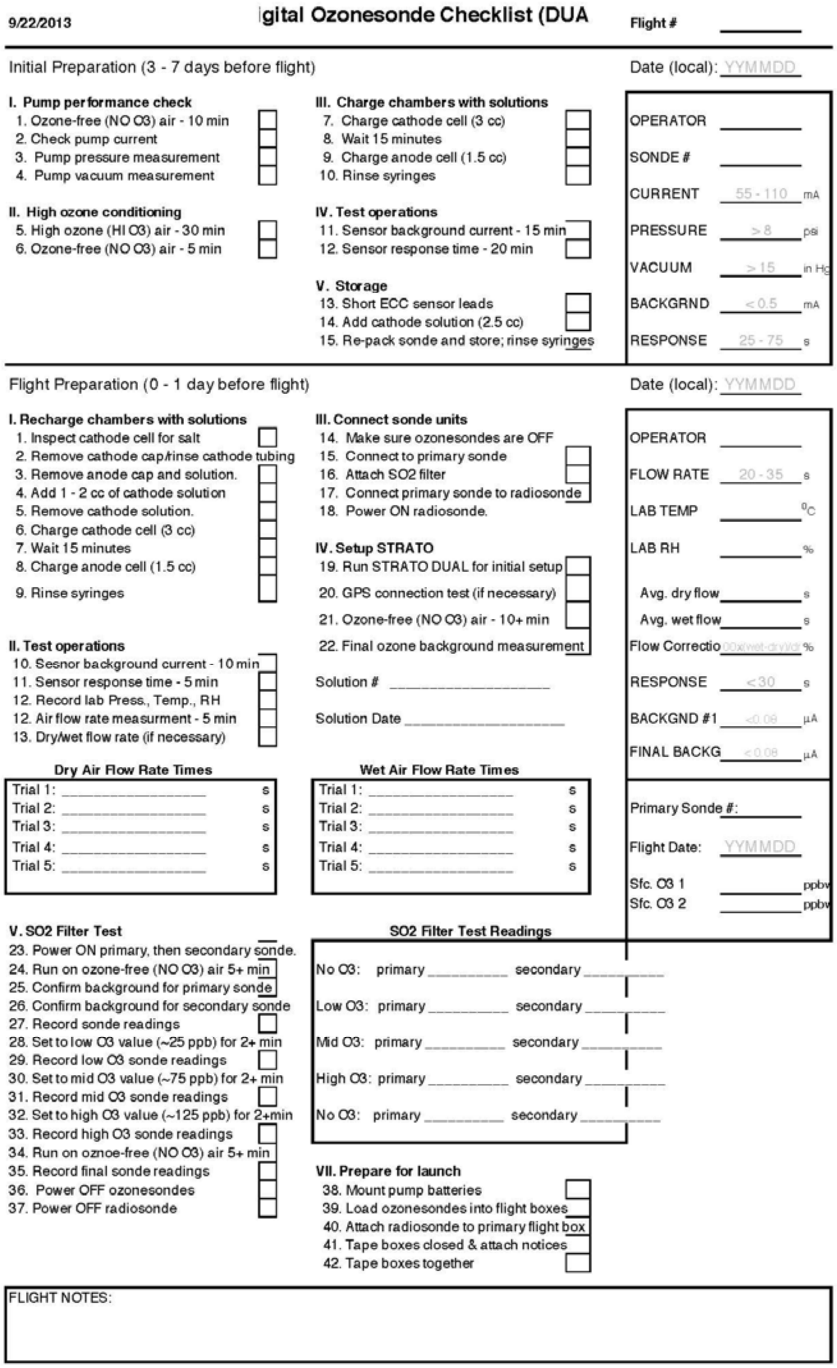
Launch Info

Elevation (m): ________________
Longitude: ________________
Latitude: ________________
Time Zone: ________________
Sfc. Pressure: Gnd. Sta. ___________ hPa
Sonde ___________ hPa
Sfc. Temp.: Gnd. Sta. ___________ ^{0}C
Sonde ___________ ^{0}C
Sfc. RH: Gnd. Sta. ___________ %
Sonde ___________ %
Sfc. O3: Gnd. Sta. ___________ ppb
Sonde ___________ ppb

IV. Post-Flight
23. Stop data recorder ☐
24. Stop Skysonde ☐
25. Turn off pre-amp & stow antenna ☐
26. Scan prepsheet ☐
27. Email data files & prepsheet ☐
28. File prepsheet ☐
29. Verify GPS alt. matches press. alt. ☐
If not, pressure offset: __________ hPa
Rerun Skysonde
30. Create plots and update website ☐

OPERATOR ________
Sky Conditions ________
Date (GMT) YYMMDD
Time (GMT) HH:MM
Time (Local) HH:MM
Balloon Type ________
Balloon Mass ________ g
Weighoff g
Fill Pressure ________ kPa
Burst Height km
Burst Press. ________ hPa
Microtops 1 ________ DU
Microtops 2 ________ DU
Satellite Col. O3 ________ DU
Sfc. O3 1 ________ ppbv
Sfc. O3 2 ________ ppbv

FLIGHT NOTES:



9/22/2013

igital Ozonesonde Checklist (DUA

Flight # ________

Initial Preparation (3 - 7 days before flight)

Date (local): YYMMDD

I. Pump performance check
1. Ozone-free (NO O3) air - 10 min ☐
2. Check pump current ☐
3. Pump pressure measurement ☐
4. Pump vacuum measurement ☐

II. High ozone conditioning
5. High ozone (HI O3) air - 30 min ☐
6. Ozone-free (NO O3) air - 5 min ☐

III. Charge chambers with solutions
7. Charge cathode cell (3 cc) ☐
8. Wait 15 minutes ☐
9. Charge anode cell (1.5 cc) ☐
10. Rinse syringes ☐

IV. Test operations
11. Sensor background current - 15 min ☐
12. Sensor response time - 20 min ☐

V. Storage
13. Short ECC sensor leads ☐
14. Add cathode solution (2.5 cc) ☐
15. Re-pack sonde and store; rinse syringes

OPERATOR ________
SONDE # ________
CURRENT 55 - 110 mA
PRESSURE > 8 psi
VACUUM > 15 in Hg
BACKGRND < 0.5 mA
RESPONSE 25 - 75 s

Flight Preparation (0 - 1 day before flight)

Date (local): YYMMDD

I. Recharge chambers with solutions
1. Inspect cathode cell for salt ☐
2. Remove cathode cap/rinse cathode tubing
3. Remove anode cap and solution. ☐
4. Add 1 - 2 cc of cathode solution ☐
5. Remove cathode solution. ☐
6. Charge cathode cell (3 cc) ☐
7. Wait 15 minutes ☐
8. Charge anode cell (1.5 cc) ☐
9. Rinse syringes ☐

II. Test operations
10. Sesnor background current - 10 min ☐
11. Sensor response time - 5 min ☐
12. Record lab Press., Temp., RH ☐
12. Air flow rate measurment - 5 min ☐
13. Dry/wet flow rate (if necessary) ☐

III. Connect sonde units
14. Make sure ozonesondes are OFF
15. Connect to primary sonde ☐
16. Attach SO2 filter ☐
17. Connect primary sonde to radiosonde ☐
18. Power ON radiosonde.

IV. Setup STRATO
19. Run STRATO DUAL for initial setup ☐
20. GPS connection test (if necessary) ☐
21. Ozone-free (NO O3) air - 10+ min ☐
22. Final ozone background measurement ☐

Solution # ____________________

Solution Date ____________________

OPERATOR ________
FLOW RATE 20 - 35 s
LAB TEMP ________ °C
LAB RH ________ %
Avg. dry flow ________ s
Avg. wet flow ________ s
Flow Correctio 00x(wet-dry)/dr %
RESPONSE < 30 s
BACKGND #1 <0.08 µA
FINAL BACKG < 0.08 µA

Dry Air Flow Rate Times

Trial 1:	________________	s
Trial 2:	________________	s
Trial 3:	________________	s
Trial 4:	________________	s
Trial 5:	________________	s

Wet Air Flow Rate Times

Trial 1:	________________	s
Trial 2:	________________	s
Trial 3:	________________	s
Trial 4:	________________	s
Trial 5:	________________	s

Primary Sonde #: ________
Flight Date: YYMMDD
Sfc. O3 1 ________ ppbv
Sfc. O3 2 ________ ppbv

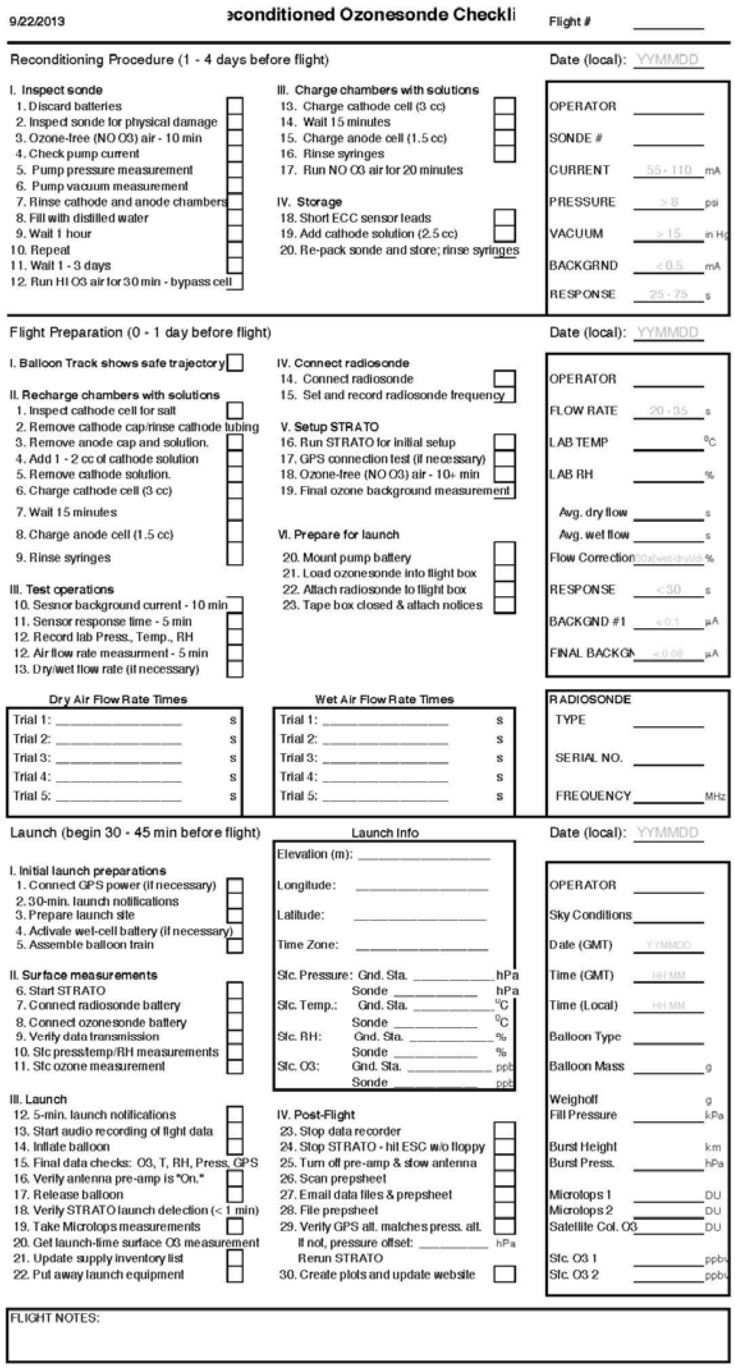
V. SO2 Filter Test
23. Power ON primary, then secondary sonde. ☐
24. Run on ozone-free (NO O3) air 5+ min ☐
25. Confirm background for primary sonde ☐
26. Confirm background for secondary sonde ☐
27. Record sonde readings ☐
28. Set to low O3 value (~25 ppb) for 2+ min ☐
29. Record low O3 sonde readings ☐
30. Set to mid O3 value (~75 ppb) for 2+ min ☐
31. Record mid O3 sonde readings ☐
32. Set to high O3 value (~125 ppb) for 2+min ☐
33. Record high O3 sonde readings ☐
34. Run on oznoe-free (NO O3) air 5+ min ☐
35. Record final sonde readings ☐
36. Power OFF ozonesondes ☐
37. Power OFF radiosonde ☐

SO2 Filter Test Readings

No O3:	primary	__________	secondary	__________
Low O3:	primary	__________	secondary	__________
Mid O3:	primary	__________	secondary	__________
High O3:	primary	__________	secondary	__________
No O3:	primary	__________	secondary	__________

VII. Prepare for launch
38. Mount pump batteries ☐
39. Load ozonesondes into flight boxes ☐
40. Attach radiosonde to primary flight box ☐
41. Tape boxes closed & attach notices ☐
42. Tape boxes together ☐

FLIGHT NOTES:



9/22/2013

conditioned Ozonesonde Checkli

Flight # ________

Reconditioning Procedure (1 - 4 days before flight)

Date (local): YYMMDD

I. Inspect sonde
- 1. Discard batteries ☐
- 2. Inspect sonde for physical damage ☐
- 3. Ozone-free (NO O3) air - 10 min ☐
- 4. Check pump current ☐
- 5. Pump pressure measurement ☐
- 6. Pump vacuum measurement ☐
- 7. Rinse cathode and anode chambers ☐
- 8. Fill with distilled water ☐
- 9. Wait 1 hour ☐
- 10. Repeat ☐
- 11. Wait 1 - 3 days ☐
- 12. Run HI O3 air for 30 min - bypass cell ☐

III. Charge chambers with solutions
- 13. Charge cathode cell (3 cc) ☐
- 14. Wait 15 minutes ☐
- 15. Charge anode cell (1.5 cc) ☐
- 16. Rinse syringes ☐
- 17. Run NO O3 air for 20 minutes

IV. Storage
- 18. Short ECC sensor leads ☐
- 19. Add cathode solution (2.5 cc) ☐
- 20. Re-pack sonde and store; rinse syringes ☐

OPERATOR ________
SONDE # ________
CURRENT 55 - 110 mA
PRESSURE > 8 psi
VACUUM > 15 in Hg
BACKGRND < 0.5 mA
RESPONSE 25 - 75 s

Flight Preparation (0 - 1 day before flight)

Date (local): YYMMDD

I. Balloon Track shows safe trajectory ☐

II. Recharge chambers with solutions
- 1. Inspect cathode cell for salt ☐
- 2. Remove cathode cap/rinse cathode tubing
- 3. Remove anode cap and solution. ☐
- 4. Add 1 - 2 cc of cathode solution ☐
- 5. Remove cathode solution. ☐
- 6. Charge cathode cell (3 cc) ☐
- 7. Wait 15 minutes ☐
- 8. Charge anode cell (1.5 cc) ☐
- 9. Rinse syringes ☐

III. Test operations
- 10. Sesnor background current - 10 min ☐
- 11. Sensor response time - 5 min ☐
- 12. Record lab Press., Temp., RH ☐
- 12. Air flow rate measurment - 5 min ☐
- 13. Dry/wet flow rate (if necessary) ☐

IV. Connect radiosonde
- 14. Connect radiosonde ☐
- 15. Set and record radiosonde frequency ☐

V. Setup STRATO
- 16. Run STRATO for initial setup ☐
- 17. GPS connection test (if necessary) ☐
- 18. Ozone-free (NO O3) air - 10+ min ☐
- 19. Final ozone background measurement ☐

VI. Prepare for launch
- 20. Mount pump battery ☐
- 21. Load ozonesonde into flight box ☐
- 22. Attach radiosonde to flight box ☐
- 23. Tape box closed & attach notices ☐

OPERATOR ________
FLOW RATE 20 - 35 s
LAB TEMP ________ °C
LAB RH ________ %
Avg. dry flow ________ s
Avg. wet flow ________ s
Flow Correction 00x(wet-dry)/d %
RESPONSE < 30 s
BACKGND #1 < 0.1 µA
FINAL BACKGN < 0.08 µA

Dry Air Flow Rate Times

Trial 1: ________________ s
Trial 2: ________________ s
Trial 3: ________________ s
Trial 4: ________________ s
Trial 5: ________________ s

Wet Air Flow Rate Times

Trial 1: ________________ s
Trial 2: ________________ s
Trial 3: ________________ s
Trial 4: ________________ s
Trial 5: ________________ s

RADIOSONDE
TYPE ________
SERIAL NO. ________
FREQUENCY ________ MHz

Launch (begin 30 - 45 min before flight)

Date (local): YYMMDD

I. Initial launch preparations
- 1. Connect GPS power (if necessary) ☐
- 2. 30-min. launch notifications ☐
- 3. Prepare launch site ☐
- 4. Activate wet-cell battery (if necessary) ☐
- 5. Assemble balloon train ☐

II. Surface measurements
- 6. Start STRATO ☐
- 7. Connect radiosonde battery ☐
- 8. Connect ozonesonde battery ☐
- 9. Verify data transmission ☐
- 10. Sfc press/temp/RH measurements ☐
- 11. Sfc ozone measurement ☐

III. Launch
- 12. 5-min. launch notifications ☐
- 13. Start audio recording of flight data ☐
- 14. Inflate balloon ☐
- 15. Final data checks: O3, T, RH, Press, GPS
- 16. Verify antenna pre-amp is "On." ☐
- 17. Release balloon ☐
- 18. Verify STRATO launch detection (< 1 min)
- 19. Take Microtops measurements ☐
- 20. Get launch-time surface O3 measurement
- 21. Update supply inventory list ☐
- 22. Put away launch equipment ☐

Launch Info

Elevation (m): ________________
Longitude: ________________
Latitude: ________________
Time Zone: ________________

Sfc. Pressure: Gnd. Sta. ____________ hPa
Sonde ____________ hPa
Sfc. Temp.: Gnd. Sta. ____________ °C
Sonde ____________ °C
Sfc. RH: Gnd. Sta. ____________ %
Sonde ____________ %
Sfc. O3: Gnd. Sta. ____________ ppb
Sonde ____________ ppb

IV. Post-Flight
- 23. Stop data recorder ☐
- 24. Stop STRATO - hit ESC w/o floppy ☐
- 25. Turn off pre-amp & stow antenna ☐
- 26. Scan prepsheet ☐
- 27. Email data files & prepsheet ☐
- 28. File prepsheet ☐
- 29. Verify GPS alt. matches press. alt. ☐
  If not, pressure offset: ________ hPa
  Rerun STRATO
- 30. Create plots and update website ☐

OPERATOR ________
Sky Conditions ________
Date (GMT) YYMMDD
Time (GMT) HH MM
Time (Local) HH MM
Balloon Type ________
Balloon Mass ________ g

Weighoff g
Fill Pressure ________ kPa

Burst Height km
Burst Press. ________ hPa

Microtops 1 ________ DU
Microtops 2 ________ DU
Satellite Col. O3 ________ DU

Sfc. O3 1 ________ ppbv
Sfc. O3 2 ________ ppbv

FLIGHT NOTES:

Addendum

In order to more completely quantify the photochemical state over the water, a photolytic NO_2 converter such as the blue light converter (BLC) from Teledyne API (previously produced by Air Quality Design (Wheat Ridge, CO, USA)) can be placed upstream of the ozone instrument sample inlet. While the BLC is typically used for photolysis conversion of NO_2 to NO for chemiluminescent detectors, it can also be used in conjunction with an ozone instrument to measure NO_2. When NO_2 is photolyzed, it forms O_3 in addition to NO. By using the BLC upstream of the O_3 instrument, the enhancement in signal when the BLC lamps are on is proportional to the ambient NO_2. Taking the difference between measured O_3 when the BLC lamps are off and O_X ($NO_2 + O_3$) when the lamps are on, ambient NO_2 can be calculated. This would directly address science questions 1-3. If the budget allows, each automated system installed on the commercial boats could be augmented with a BLC, LabJack U3-HV, and associated plumbing and electrical connectors. Additional calibration and instrument characterization would be required, but can easily be performed in the labs at UH as well as in the field during quarterly calibrations. No additional calibration supplies would be needed for this project. The same equipment would be used to characterize the NO_2 conversion of this system as is used to characterize and standardize the NO_2 measurements as part of the UH HNET system, allowing for direct comparisons to other NO_2 monitors, such as the one deployed during ozone season to Smith Point (C1606).