ENVIRON

MEMORANDUM

To: NETAC Technical Committee

From: Greg Yarwood and Sue Kemball-Cook

Date: February 19, 2010

Subject: Proposed HRVOC Monitoring at Longview in August-September, 2010

SUMMARY

NETAC's FY10/11 draft workplan includes Task 3 to conduct "Seasonal Ambient Monitoring" with a budget of $200,000. The purpose of the ambient monitoring is to improve our understanding of the types and sources of highly reactive VOCs present in the vicinity of Longview as well as the role that these VOCs play in ozone formation. The first proposed task is monitoring for total highly reactive volatile organic compounds (HRVOCs) at CAMS 19 in August and September 2010 with a budget of $105,000. Data will be collected by Washington State University, analyzed by the University of the Houston and ENVIRON, and documented in reports to NETAC in the fall of 2010.

BACKGROUND

In recent years, NETAC has collected canister VOC samples at CAMS 19 to augment the TCEQ's monitoring activities at Longview. During August-October, 2008, NETAC carried out a successful monitoring program which confirmed the presence of intermittent plumes of highly reactive VOCs (HRVOCs) at CAMS 19. HRVOCs were analyzed using a reactive alkene detector (RAD) which made a measurement once every second, 24 hours a day, providing a nearly continuous record of HRVOCs at CAMS 19 over a 2 month period. The high time resolution RAD data confirmed the intermittent character of the HRVOC impacts (i.e., HRVOC spikes) and showed that HRVOCs were present on a significant fraction of days, with 10 of 64 sampled days showing strong RAD signals above 30 ppb. The natural background for HRVOCs (i.e. biogenic HRVOCs whose primary constituent is isoprene) at CAMS 19 may be expected to be approximately 10 ppb at midday.

NETAC has investigated the relationship between periods of high ozone and high HRVOC levels at CAMS 19 during August-September, 2008. Many periods of high HRVOC levels were not associated with high ozone at CAMS 19; most of these occurred at night. Some days with HRVOC spikes may not have been conducive to ozone formation (lower temperatures, clouds). However, high 1-hour ozone values coincided with HRVOC spikes on 3 days in September showing that HRVOC spikes could influence the attainment status of CAMS 19. The wind direction during HRVOC spikes suggests that the nearby Eastman Complex (comprised of the Eastman, Westlake and Flint Hills chemical companies) is the source.

NETAC modeling suggests that the HRVOC emissions needed to produce the observed HRVOC spikes at CAMS 19 are greater than are found in the Eastman Complex typical day emission inventory. Potential causes of such high emissions are not readily apparent. Estimates of the Eastman Complex ethene (HRVOC) emissions derived from a 2006 NETAC aircraft flight are consistent with the TCEQ 2005 emission inventory for a typical ozone season day. The Eastman Complex operators have indicated that such large HRVOC releases seem unlikely without detection by their control and/or safety instrumentation. Therefore, the origin of the HRVOC spikes at CAMS 19 remains unclear. A method for addressing this uncertainty is to undertake additional HRVOC monitoring during 2010 using event-triggered canister data sampling.

In event-triggered canister sampling, a continuously-operating HRVOC detector monitors the ambient air; when the measured HRVOC levels are above a threshold value, a canister is opened and ambient air is pumped into the canister for a pre-determined time period in order to sample the HRVOC plume. At the end of the sampling time period, the canister is sealed and then taken to a laboratory and analyzed in order to determine the chemical composition of the sample. Analysis of canister samples taken during HRVOC spikes will allow chemical fingerprinting of the source(s) of the spikes that can further our understanding of high HRVOC/ozone events at CAMS 19. As in August-September 2008, HRVOC data collection will be carried out by Tom Jobson, Gene Allwine, and Shelly Pressley of the Laboratory for Atmospheric Research at Washington State University (WSU). The laboratory canister sample analysis will be performed by Bernhard Rappenglueck of the Department of Earth and Atmospheric Sciences at the University of Houston (UH).

STATEMENT OF WORK

Instrumentation for carrying out event-triggered canister data sampling of HRVOCs will be configured and installed at CAMS 19 by WSU. A rapid alkene detector (RAD) will be used to acquire total alkene mixing ratios for the August-September 2010 time period, as was done during the August-September 2008 CAMS 19 study. The RAD signal will be used to trigger NETAC's Entech canister autosampler to collect air samples when the total alkene signal reaches a threshold value. The autosampler opens the canister and pumps in ambient air. At the end of the pre-set sampling time, the autosampler seals and removes the canister, and loads a new canister for the next high HRVOC event.

Based on the RAD data acquired during 2008 at CAMS 19, we propose to collect 24 canister samples over the August-September 2010 sampling period. Canister fill times of about 10-15 minutes will be required to sample high alkene plumes. High alkene events are nominally defined here as total alkene (RAD) mixing ratios > 30 ppb, and the autosampler will be configured to trigger canister collection when the measured mixing ratio exceeds this value. For the 2008 study with the RAD at CAMS 19, approximately 12 such events were observed of various time durations. Figures 1 and 2 show two high HRVOC events from August-September 2008 and illustrate the event-triggered canister sampling method to be used in the 2010 study.

The RAD data points in Figures 1 and 2 are 1 minute apart and a black vertical line is drawn through the first data point that has a RAD value >30 ppb; this is the point at which the canister sampling would begin if the event were to occur during the 2010 study. The red arrows show the duration of the sampling if the canisters are filled with ambient air over the course of 10 minutes, and the green arrows show a 15 minute sampling period. In Figure 1, both a 10 minute sample and a 15 minute sample would collect ambient air throughout the time when HRVOC concentrations are elevated above 30 ppb. A single canister would therefore suffice to characterize the event. A second canister would be taken once the RAD value dropped back below the 30 ppb threshold. The right-hand vertical black line indicates when this canister would begin sampling. The purpose of the second canister is to collect ambient background air outside the HRVOC plume to assess the HRVOC enhancement during the event.

Figure 2 shows an example of an event with longer duration. On September 19, 2008, the RAD values remained above 30 ppb for about half an hour. In the 2010 study, the autosampler will be configured to fill a second canister if the RAD reading is greater than 30 ppb at the end of the ambient air collection for the first canister, and so on until the RAD value drops below 30 ppb. For event like the one shown in Figure 2, three canisters would be collected if the sampling time is 10 minutes, and two canisters would be filled using a 15 minute sampling time. The sample duration also will depend upon how rapidly the pump is able to fill a canister. Sample duration will be decided after laboratory testing the auto sampler. As in Figure 1, the right-hand vertical black line shows when sampling begins for the canister that samples the background air.

The canisters will be supplied by UH, who will perform the canister analysis. UH has conducted similar analyses for recent TCEQ-sponsored projects. Before the sampling period begins, UH will ship canisters to WSU for testing of the sampling unit, and UH will prepare and ship 24 2 valve, 1 liter canisters to Longview for use in the study. WSU will modify the RAD to trigger canister collection and test its performance before deployment. WSU will be responsible for deploying and operating the RAD and canister sampling system at CAMS 19, performing QA/QC of the RAD data, supplying the RAD data in electronic format to NETAC, and shipping the filled canisters to UH. UH will then perform C2-C9 VOC analysis of the canisters at the UH laboratory using GC-FID. An additional 6 canisters will be used for QA; 3 canisters will be used for zero tests and 3 canisters will be used for a standard recovery test. UH will provide documentation of the analysis results in electronic format (e.g., a spreadsheet).

RAD Modification

WSU will modify the data acquisition system of the RAD to provide an external output to trigger the Entech canister sampler. This will require using an additional software and hardware data acquisition package (Azeotech + Labjack). WSU has used this combination of software and hardware for other instruments, so this will be a relatively easy transition. The system will be tested at WSU to make sure the canisters are filled correctly (i.e. short fill times, high enough pressure). This will likely require replacing one of the mass flow controllers in the Entech sampler with a higher flow rate mass flow controller to ensure shorter fill times. Based on the canister sizes to be supplied by UH and the desired sample pressure, WSU will determine the appropriate flow controller size. WSU will test the canister fill system for cleanliness and alkene artifacts at WSU by filling canisters with zero air and analyzing them by GC-FID. The data acquisition system of the RAD will also be modified to record the trigger events, so that date and time of canister sampling are known.

Installation of Equipment at the Longview CAMS 19 Site

Instrumentation necessary for monitoring total alkenes includes the rapid alkene detector (RAD), ozone generator, laptop computer, calibration valve control unit, analog to digital converter, uninterruptable power supply (UPS), calibration standard, and liquid oxygen tank. All equipment (except for the liquid oxygen cylinder) will be located inside the CAMS 19 trailer and will be installed by WSU.

The inlet to the RAD will be ¼" Teflon tubing extending through a hole in the CAMS 19 trailer wall with an inlet to prevent water collection. The liquid oxygen tank will be delivered to the site by a local gas distributor. The tank will sit on a plywood base and be secured via cables and metal stakes into the ground to prevent the tank from being tipped over. Gaseous oxygen will be delivered to the RAD via copper tubing and/or Teflon tubing depending on the distance. Exhaust from the RAD will be scrubbed of ozone during a three stage process. The first stage is the catalytic converter within the RAD which is heated to 380°C; the second stage is an activated charcoal trap, and in the third stage, the exhaust will be transported via a 50 foot-long garden hose through a hole in the floor of the trailer and away from the trailer. This equipment configuration was used successfully during the August-September 2008 sampling period, and will guarantee no interferences with existing ozone monitoring instrumentation at this site.

Space will also be required for the canister sampling system. Counter or rack space for two 19" wide electronics boxes that constitute the Entech canister sampling system plus additional space for canisters will be required.

Operation and Remote Monitoring

The system will run continuously with the exception of power outages or other unforeseen problems. Calibrations will be done automatically with the use of a timer programmed to perform calibrations twice each day. Calibration times will vary from day to day so that missing data periods are not at the same time each day. The schedule for each calibration includes an initial zero of the instrument, followed by a calibration using a standard of choice, and ending with another zero. Total time for each calibration is 10 minutes.

Data acquisition will be accomplished using AzeoTech DaqFactory data acquisition software to record the various flow rates and photomultiplier tube count rates from the RAD and to provide the external events trigger for the canister sampler. Raw data files are stored every 30 minutes on the PC, thus a power outage may only result in the loss of the previous 30 minutes of data. The use of a MS Windows-based program allows remote monitoring via the Remote Desktop program. Using a Sprint Card for wireless internet access, Remote Desktop will be used to monitor the RAD and transfer data files. In the event of a long-term power outage (longer than the UPS can sustain), the RAD and computer may need to be restarted. Brief power outages should be manageable with the UPS.

WSU will require on-site assistance on a weekly basis to ship filled canister samples by FedEx to the analysis lab. Such a person has been identified. A part-time employee working for the University of Texas on their THMHC sampling project at CAMS 19 could potentially be made available by UT.

Data Reduction and Final Reporting

One minute average total alkene mixing ratios will be determined for the duration of the two month sampling period with the exception of calibration periods, power outages, or other unforeseen problems. Calibration coefficients will be applied to the raw count data to determine mixing ratios. Missing data periods (i.e. calibration periods, power outages etc.) will be indicated with -999. The raw data files in a txt format (30 minute files), plus the final mixing ratio files (either txt, Igor, or MS Excel files) will be provided in the final report. A log of canister sampling times will be provided. A copy of the site logbook with operating notes during operation, data reduction notes will also be included in the final report. Further analysis of the data (i.e. diurnal patterns or concentrations as a function of wind direction, etc.) is not included in WSU's scope of work and will be carried out by ENVIRON.

UH will perform C2-C9 VOC analysis of the canisters at the UH laboratory using GC-FID and will provide documentation of the analysis results in electronic format (e.g., a spreadsheet).

ENVIRON will be responsible for the final reporting on the study to NETAC.

Table 1 lists the project timeline and project milestones.

Table 1. Project Timeline

Task	**Date**	**Comments**
Prepare instruments	June-July	Replace mass flow controller
Purchase calibration gases	June	
Write QAPP for TCEQ approval	June	Completed QAPP submitted to TCEQ by July 7, 2010
Conduct calibration and sensitivity tests	July	Determine response factors for isoprene, ethene, propene
Install RAD and autosampler @ CAMS19	July 29-31	Site visit coordinated with TCEQ instrument operator
Field Measurements	Aug 1 – Sept 30	One site visit planned
Remove Equipment	Oct 1-2	Site visit
Data QA/QC and reporting	Oct 5- 30	WSU, UH, and ENVIRON

Project Staff

Data collection and quality assurance will be performed by WSU and data analysis and interpretation will be performed primarily by ENVIRON. Canister VOC data analysis will be carried out by UH. The key project staff are as follows:

Tom Jobson (WSU) – PI, general oversight, setting up the external events triggering of the can sampler, remote monitoring of instruments, report writing.

Gene Allwine (WSU) – primary responsibilities will involve setting up the RAD to trigger the canister sampler, testing the system, preparing the instruments for field deployment, installation and site visits at the CAMS 19 field, remotely monitoring system, help with QAPP and final report preparation.

Shelley Pressley (WSU) – primary responsibilities will involve RAD instrument set-up, laboratory testing and calibrations of the RAD, remote monitoring of instruments, final data preparation, and report writing.

Bernhard Rappenglueck (UH) – supply canisters and perform canister sample analysis.

UT Employee (UT) – remove filled canisters from autosampler and ship canisters to UH.

Sue Kemball-Cook (ENVIRON) – data analysis and interpretation relying on HRVOC and canister data collected by this project as well as other monitoring data obtained by TCEQ at CAMS19 and results from previous NETAC studies.

Greg Yarwood (ENVIRON) – overall principal investigator for the project and responsible for communications with TCEQ and NETAC.

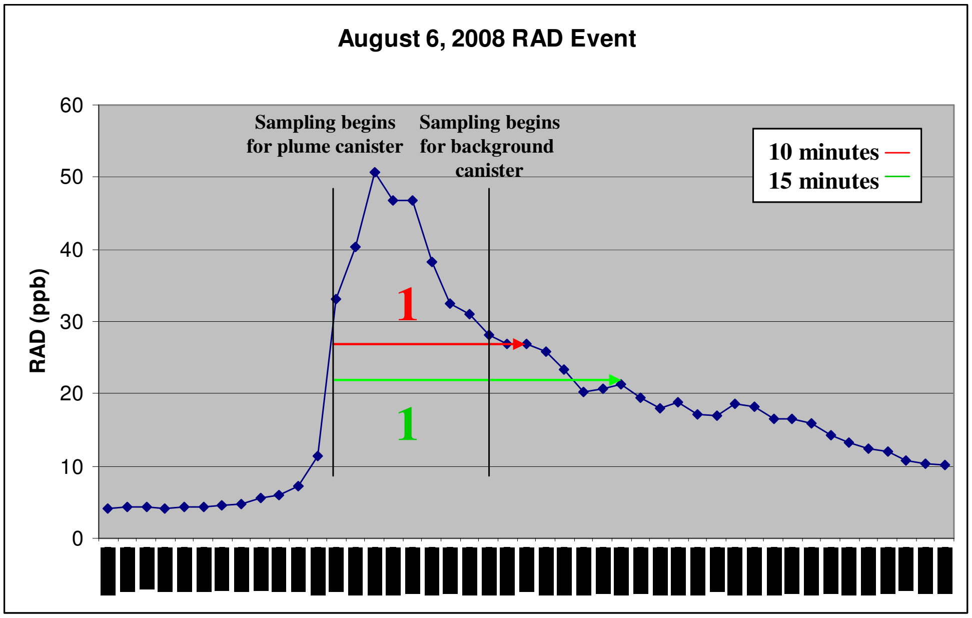

Figure 1. Time series for the August 6, 2008 high HRVOC event showing the RAD mixing ratio at one-minute intervals. Left vertical black line shows when canister sampling would be triggered if this event occurred during the 2010 study. Red line indicates the time period when a canister would be open to sample the HRVOC plume for a 10 minute sampling period. Green line shows duration of 15 minute sample. Right vertical black line shows time when a second canister would begin sampling the background air outside the HRVOC plume.

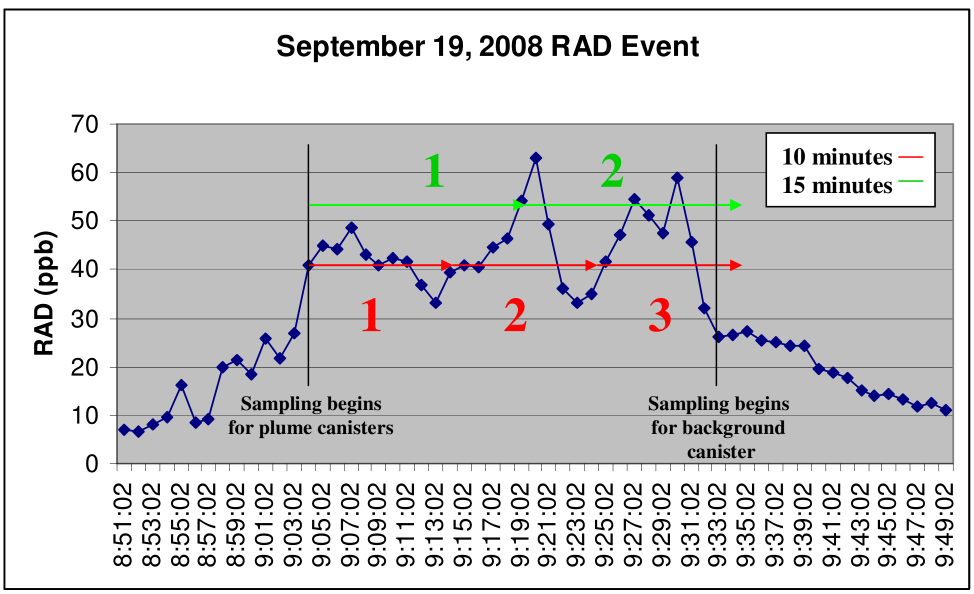

Figure 2. Time series for the September 19, 2008 high HRVOC event showing the RAD mixing ratio at one-minute intervals. Left vertical black line shows when canister sampling would be triggered if this event occurred during the 2010 study. Red line indicates the time period when a canister would be open to sample the HRVOC plume for a 10 minute sampling period. Green line shows duration of 15 minute sample. Because the event lasts for more than the sampling duration of a single canister, the sampling time for each required canister is shown. For a 10 minute sampling period, 3 canisters would be taken to sample the HRVOC plume. For a 15 minute sampling period, 2 canisters would be taken to sample the HRVOC plume. Right vertical black line shows time when a canister would begin sampling the background air outside the HRVOC plume.