

**Top-down Verification of Sweeny VOC Emissions  
Based on the Sweeny Tracer Study 2003**

**FINAL REPORT**  
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Submitted by

**Noor V. Gillani, PI**  
**Yuling Wu, Co-I**

Earth System Science Center  
University of Alabama in Huntsville (UAH)  
Huntsville, AL 35899

Submitted to

**Dr. Alex Cuclis, Project officer**  
Houston Advanced Research Center  
4800 Research Forest Drive  
The Woodlands, TX 77381

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## EXECUTIVE SUMMARY

Under HARC Project H-26, UAH has performed a variety of top-down emissions verification (TDEV) analyses of the data of the Sweeny Tracer Study 2003 (STS-03) conducted during mid-November to mid-December 2003. The study was motivated by the HARC H-26 project of Brookhaven National Lab. (BNL), the primary goal of which was to release two different artificial perfluorocarbon tracers (PMCP and PDCB) at known rates from the Sweeny refinery-petrochemical plant in Brazoria CO (southwest of Houston), then sample them in canisters aboard the Baylor Aztec aircraft, in the Sweeny plume downwind, along with concurrent canister measurements of speciated VOC, and continuous measurements of NO<sub>y</sub>, ozone and reactive alkenes (Reactive Alkene Detector, RAD), in order to estimate the emission rates of ethene and propene from Sweeny based on application of the tracer method of TDEV. In this report, UAH has reviewed and assessed the BNL results of the tracer study, and has also applied the following three other methods of TDEV to the data of STS-03 : (a) the ratio method using the canister data as well as the continuous data (RAD) of the VOC relative to the continuous data of NO<sub>y</sub>; (b) the flux method; and (c) the diagnostic modeling method based on application of UAH-LESchem.

STS-03 consisted of two controlled tracer releases from Sweeny during the daytime on four separate days (Nov. 20, 25 and December 7, 14), and coordinated aircraft sampling upwind (~3-5 km) and downwind (1.5 – 30 km) of Sweeny, involving mainly upwind and downwind spirals (vertical soundings) and downwind crosswind plume traverses in 7-8 downwind plume cross-sections. In particular, in 2-3 downwind cross-sections within 10 km of the source, there were multiple plume traverses at different heights within the CBL, while there were only single plume traverses at farther downwind cross-sections. Aircraft measurements included continuous measurements of NO<sub>y</sub>, CO, ozone, RAD (a basically uncalibrated continuous alkene monitor), Bscat (multi-wavelength), the navigational variables LAT/LON, altitude, and the meteorological variables T, RH and WS/WD. Measurements were also made alternately of NO and NO + photolysed NO<sub>2</sub> (following passage through a photocell) using a single NO<sub>x</sub> analyzer, with periodic switching between the two modes. Other measurement platforms included the University of Houston (UH) sodar (near Dancinger less than 10km north of Sweeny) for winds up to about 600m and the Ellington profiler nearly 100km away in a coastal environment, and surface met/chem measurements (including net radiation and auto-GC for continuous speciated VOC) at the Dancinger surface monitoring site (CAMS 618).

A number of data-related problems have been identified in our examination of the data. In a plume study with special focus on measurements in the near-field range from the source, use of a single instrument to measure NO and NO<sub>2</sub> was a mistake and has resulted in both NO and NO<sub>2</sub> data becoming more or less useless. Also, the practice of performing auto-zeros in the aircraft have resulted in loss of critical plume data of NO<sub>y</sub> and RAD in several plume traverses. The sodar measurements were made only *prior* to the aircraft measurement times and *not* during the flight times, resulting in absence of that critical dataset in the analysis also, leaving only the aircraft data of winds (the Ellington profiler was too far away, and in a coastal environment, such that the data were unsuitable for extrapolation to the inland conditions near Sweeny). The aircraft data of winds are valid only during straight flights, causing loss of much of the aircraft wind data. Also, these being continuous, they were subject to gusts, making it difficult to assess the contribution of unsteady winds to the uncertainty of the analyses, especially in the flux

method and the diagnostic modeling method. There were some other troublesome practices in the aircraft flights also: some traverses were not long enough to capture the full plume; the downwind spirals were horizontally too large to remain continuously within the plume, thereby failing to provide continuous vertical soundings in the plume; on two of the four days, the spirals were not high enough to adequately capture the elevated inversion capping the mixing layer in order to provide the critical information about the mixing height.

The reliability of VOC emissions estimates based on the tracer method and the ratio method, using the very discrete and sparse canister data, is particularly subject to the validity of the explicit assumption in the method that the tracer and the target VOCs are co-emitted. This is particularly true when the ambient measurements of the tracers and the VOCs are very close downwind of the spatially inhomogeneous source of the emissions. UAH explored the validity of the co-emission assumption by plotting in detail the 3D spatial distribution of the many VOC and NO<sub>x</sub> sources at Sweeny (based on the emissions inventory, EI, information) along with the locations of the tracer releases. Within a range of about 300m horizontally (about the size of the Sweeny plant), the assumption of VOC and tracer co-emissions does *not* appear to be very good; also, there is a significant disparity in the vertical distributions of the VOC, NO<sub>x</sub> and tracer releases. The concurrent downwind VOC and tracer measurements were made typically 3-7 km from the source on winter days (limited mixing intensity) when there was still a significant signature in the ambient crosswind plume concentrations of the spatial separation of the emissions. There were a maximum of only two downwind canister samples per flight mission (a total of seven over the four days), and in two of them there was no significant plume encounter, and at least one canister sample was in a valley between two RAD peaks. Consequently, the sample size of the “good” plume samples (4 over all 4 days) is extremely meager, and the inferred emission rates of ethene and propene must be considered to be very spotty and lower-bound estimates, at best. The inferred emission rates by the various methods are summarized in Table 4. The VOC emissions on 12/7 were, evidently, *much* higher than on the other days. For these other days, the tracer method gave an estimate of  $Q(\text{NO}_x) \sim 5.1 \text{ kmol/h}$ , compared with the annualized EI value of 12 kmol/h, and gave  $Q(\text{ethene})/Q(\text{NO}_x) \sim 0.76$ , and  $Q(\text{propene})/Q(\text{NO}_x) \sim 0.4$ . The application of the ratio method (the ratios of VOC/NO<sub>y</sub> were of plume excess concentrations over background values) based on the canister data for VOC resulted in 3 (out of 7) negative values because the upwind (background) value was higher than the downwind (presumed) plume value for either NO<sub>x</sub> or VOC in these samples. Excluding 12/7, the “good” estimates of  $Q(\text{ethene})/Q(\text{NO}_x)$  are between 0.5 and 0.9, and of  $Q(\text{propene})/Q(\text{NO}_x)$  are between 0.2 and 0.4, in reasonable agreement with the tracer method result. The emissions estimates for 12/7 based on the canister data were about an order of magnitude higher.

Given the paucity of the canister data, we have tried to utilize the continuous RAD data in a quantitative manner by trying to calibrate it based on known sensitivities of RAD to different alkenes (e.g., quite sensitive to propene, but much less to ethene). We have developed a calibration of RAD which gives us estimates of propene from it, albeit with a factor of two (or more) uncertainty. The RAD and NO<sub>y</sub> ratios were based on their crosswind integrated plume traverse values in excess of the local measured backgrounds. Using RAD as a quasi-surrogate for propene, the ratio method gives quite a wide variability of the ratio for different traverses in the same plume cross-section (again giving much higher values of VOC/NO<sub>y</sub> for 12/7). Averaged over the plume cross-section,  $Q(\text{propene})/Q(\text{NO}_x)$  was within  $1.10 \pm 0.24$  for 11/25

for both the ratio method and the flux method (based on RAD), and within  $1.68 \pm 0.58$  for 12/14, and again significantly higher for 12/7. The results of the ratio and flux methods using the RAD and NOy data are quite consistent with each other.

The database was most complete for 11/25, and for that day, two estimates of the NOx emission rate by the flux method were 13.2 and 11.1 kmol/h, compared to the 2002 EI value (believed to be fairly accurate) of 12 kmol/h. Thus, the flux method, given adequate continuous data, may be a fairly reliable approach for TDEV. However, even by the flux method, the inferred emission rates of NOx for the four days ranged between 3.4 and 13.2 kmol/h, indicating a possible significant day-to-day variability in Sweeny emission rates, not only of VOC, but also of NOx. For 11/25, the emissions of ethene and propene appear to be comparable to the NOx emission, within a factor of 2-3.

Our overall major conclusion based on the purely empirical methods is that TDEV based on very spotty canister measurements is quite un-satisfactory. It is necessary to have continuous ambient data. The availability of the PTR-MS continuous and speciated VOC data in TexAQS-II should be of major importance to permit meaningful experimental design. Unfortunately, the inability of PTR-MS to measure ethene will be a very significant shortcoming. Appropriate use of an FTIR or other system should be considered in the future, to measure ethene.

All of the purely empirical methods of TDEV neglect the effect of depletion of the target primary species by chemistry and removal processes and also circumvent the effect of plume dispersion in the tracer and ratio method by resorting to the (unjustified in this case) assumption of co-emission. Only the diagnostic modeling method explicitly includes the treatment of these processes in detail. There is overhead here, however, in that more input information is needed related to the processes of dispersion and chemistry. Such needed input information was substantially absent in STS-03. The detailed simulation of plume physics at very high spatial-temporal resolution was very revealing of the complex reality, particularly in the near-source regime from the source, where very unsteady and complex plume behavior is evident (e.g., plume looping and meandering). Any data-model comparisons in this regime are judged to be very tenuous based on instantaneous measurements. It is recommended that the measurements be removed from the emission source by at least 15 minutes of transport ( $\sim 1$  km for each unit of WS in m/s).

*For an optimum TDEV study TDEV of industrial point source complexes, we recommend implementation of a combination of the ground-FTIR-based solar occultation flux method (Mellqvist, 2004) to capture all plume flux, and the aircraft measurements to provide details in the vertical direction (critical to determine reasonably accurate linking of the wind data to the ambient concentration data). The aircraft data would also serve to evaluate the resulting emission rate. An equally important measurement, poorly covered in STS-03, is the accurate measurement of wind speed near the emission source.*

All in all, there were many shortcomings in STS-03, but this analysis has revealed many matters which will contribute strongly to better planning and execution of TDEV experiments in TexAQS-II. The outlook for a successful TDEV study in TexAQS-II is quite good, but success will require very careful planning and execution. In particular, the planning will need to include

considerations of the requirements of diagnostic modeling (LESchem in the near-field and LRPM farther downwind), the only TDEV method which can include the roles of transport and chemistry explicitly, and also of the spatial-temporal detail of the emission field.