

FINAL REPORT
Hydrocarbon Measurements for
TVA 2005

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General

111 ambient air samples were taken by TVA during flights in the summer of 2005. Seven canisters were filled for quality assurance. These canisters were supplied by York University. 126 canisters were leak tested, cleaned and evacuated before they were shipped to TVA. There were 9 canisters (including TVA10), which were returned empty. This final report presents the results of the measurements for all the 118 canisters (from TVA1 to TVA111 and QA-A to QA-G). Errors, reproducibility, uncertainty estimates and details of detection limits are also present in this report.

About 100 NMHC were quantitatively determined in each of the air samples using state-of-the-art chromatographic analysis. The results presented in this report should be considered final, however, evaluation and verification of the methodology is ongoing. Although unlikely, it cannot be excluded that this may result in minor changes for some of the reported data. It should also be noted that the samples contained a number of unidentified compounds at trace levels. The original chromatograms are archived at York University and re-evaluation will be possible if deemed necessary.

Sampling and storage

The samples were collected in stainless steel canisters (internally electropolished by the SUMMA® process) equipped with stainless steel metal bellows valves. The canisters were cleaned, evacuated and shipped to the location specified by TVA. For most hydrocarbons, the concentration does not change by storage in the canisters. For light alkenes (C₂-C₄), formation of artifacts can be observed. Artifact formation in the

canisters may be significant for low alkene concentrations. Although generally artifact levels are in the pptv range, it has to be remembered that this artifact problem can result in very significant uncertainties for some of the reported levels of light alkenes. It is important to note that there is no indication for the existence of an artifact problem for isoprene.

For 16 samples the measurements were repeated within a time period ranging from less than one day to 40 days. The average time period between first measurement and repeat was 15 days. This allowed testing the samples for an increase of alkene concentrations with time. The concentrations of ethene increased on average by 10%. The corresponding values for propene, 1-butene, i-butene, and 1-pentene are 5.4%, 6.7%, 4.3% and 6.4%. These changes are relatively small, but it also should be noted that they have a considerable uncertainty which allows for upper limits in the low pptv range. Since on average the time intervals between repeat measurements are comparable to the time lag between sampling and measurement, the values above provide a reasonable estimate for the upper limit of artifact formation during sample storage. However, since none of the samples could be analyzed within less than a week after sampling, the results given above does not necessarily limit possible artifact formation during or immediately after sampling.

Analysis

When received, the air samples were diluted with Helium (UHP-Alphagas1) by a factor between 2 and 3 (please refer to enclosed excel file). Relative pressures before and after dilutions were taken and corrected to absolute by using the atmospheric pressure provided by MSC (Meteorological Service of Canada) on the day of dilution. Air samples were allowed to stay two or three days for complete mixing.

The air samples were analyzed on two gas chromatographs, each equipped with a flame ionization detector (GC-FID). The separation in each GC used a different column; an aluminum oxide porous layer open tubular (PLOT) column and a DB-1 wall coated open tubular (WCOT) column. Prior to separation, the hydrocarbons in the samples were concentrated from (typically) 0.8 liter (STP) of the air-helium mixture by a two step cryogenic enrichment procedure. Peak identification is based on retention time and

established by comparison with standards. In total about one hundred different hydrocarbons in the range from C₂-C₁₀ are determined with the two-GC analysis.

The measurements were evaluated quantitatively by comparison with a reference gas (calibration standard) of known composition and taking into account the dilution of the samples. It is estimated that the hydrocarbon concentrations in the calibration gas are accurate within 5%.

Detection limits, reproducibility and accuracy

The lower limits of detection for both GCs (3σ) are generally around 2-3 pptv. However, due to the primary dilution, the limits of detection are around 6 pptv for the samples. With this slightly reduced detection limit, we have therefore chosen to report values below 5 pptv as LDL (Lower Detection Limit), indicating that the peak area is below the estimated detection limit. For concentrations well above the lower limit of detection the reproducibility of the measurements is between 2% and 5% depending on the compound. This is verified for each set of samples by randomly selecting approximately 10% of all samples for repeat analysis. Furthermore, the samples are analyzed on two different GCs, and there are hydrocarbons which are analyzed on both instruments. These results are checked for consistency; in case of discrepancies the measurements were repeated. For mixing ratios near the lower limit of detection the errors increase to between 10% and 30%. For those compounds where both instruments allow interference free detection, both instruments agree within the uncertainty of the measurements.

The accuracy of the calibration has been checked by several informal comparisons with other laboratories as well as by participation in the NOMHICE intercomparison and the intercomparison study performed as part of the Houston 2000 field campaign. From the results of these comparisons we conclude that our calibration is generally correct within better than 5%.

Results

The results are summarized in the attached table. For those compounds where both GCs allowed interference free detection the average of the two measurements is

reported. Similarly, for samples analyzed twice the given values are the average of the two measurements.

There are data points, showing overlaps with unidentified peaks, baseline problems or small artifact peaks. This prevents meaningful determination of mixing ratios. These are indicated by N/A (Not Available). In most of the cases, with the exception of a several cyclo-pentane and 2-me-2-butene measurements, the overall peak area is small and it seems safe to assume that in these cases the mixing ratios are in the lowest pptv range or below. For cyclo-pentane and 2-me-2-butene however, the artifact sometimes is substantial.

Since the peak area of n-decane in the blank runs is highly variable, it is not possible to determine meaningful n-decane concentration for any of the samples.

In one sample (TVA4) there is a surprisingly high value for toluene. There is a possibility of sample contamination due to canister leakage. Although leak tests were performed prior to shipping the canisters for all canisters, it cannot be excluded that a leak has developed from handling the canisters. The canisters will be tested for leakage after, but for obvious reasons this is the last step in the procedure since leak testing will result in loss of any remaining sample, preventing any further tests for analytical problems. At present we have no reason to exclude this value; toluene results from both GCs agree very well and there is no indication for peak overlaps or retention time shifts, which would justify removal of this measurement from the data set. Similarly, for the high mixing ratios found in some samples for several terpenes, we have found no indication of peak overlaps or other indications of analytical problems. However, it should be noted that terpene data are only available for one separation column and therefore the possibility of peak overlaps cannot be ruled out. It is known that the retention times for some heavier alkyl benzenes are very similar to those of several of the terpenes analyzed here.