Total Non-Methane Organic Carbon: Measurements of Total and Speciated Hydrocarbons at Azusa, California

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Introduction

The formation of ozone and other oxidants in urban and rural areas remains a persistent problem that affects both the public health and economic vigor of many areas around the globe. Oxidant formation results from photochemistry of organic compounds in the presence of nitrogen oxides. The organic component begins mainly as non-methane hydrocarbons (NMHC, containing only carbon and hydrogen) from biogenic and anthropogenic sources. These compounds are progressively oxidized to CO and CO_2 over periods of hours to weeks. The variety of primary hydrocarbons and their oxidation products is large. While separate techniques exist to measure groups of compounds (e.g., C_2-C_8 hydrocarbons with some oxygenates, or alcohols, or formaldehyde or organic nitrates, etc.) no techniques to assess the total loading of non-methane organic carbon (TNMOC) have been widely applied in the atmosphere. The goal of this work is to determine the relationship between the total non-methane organic compounds and the sum of the speciated volatile organic compounds (VOC's) measured by standard techniques. The primary scientific motivations are to define the airborne quantity of reactive organic carbon, find how close this quantity is to the standard measurements of VOC's, and address the question of what happens to the multifunctional products of the photo-oxidation reactions of emitted hydrocarbons; do they stay in the gas phase or are they removed to the aerosol phase or surfaces?

There are several reasons to expect the TNMOC measurement to result in a number that is larger than the sum of the routinely measured VOC's. Loss of oxygenated and semi-volatile compounds in sampling and on columns is well known [1, 2], although the extent of the losses is very difficult to quantify. Modeling results indicate that while the initial oxidation step of a hydrocarbon may take place within hours, if our understanding of the relevant processes is correct, complete removal of the partially oxidized fragments should take weeks [3]. Finally, in controlled smog chamber photooxidations, a standard gas chromatograph with flame ionization detection (GC/FID) measurement can account for much less than 100% of the reacted parent hydrocarbon [4]

Roberts and co-workers have developed a column back-flush approach to make a TNMOC measurement in ambient air [5]. This approach has the advantage of achieving quite low detection limits (~1 ppbv) but may lose semi-volatile compounds to the GC column. Roberts et al. (1998) compared their TNMOC concentrations with speciated VOC measurements collected by other groups with instruments nearby to calculate the TNMOC/· speciated VOC's ratio. Since the calibrations, sampling frequencies and averaging times were different, a fair degree of scatter is anticipated, and a systematic error is possible. Measuring in relatively clean air in Boulder, Colorado, and Nova Scotia, Canada, they found differences between TNMOC (which they refer to as "C_y") and the sum of hydrocarbons and carbonyls that were small in absolute terms (averaging 3.8 ± 7.9 ppbC) but were significant in percentage terms. Ratios of

TNMOC/· speciated hydrocarbons + carbonyls were 1.36 ± 1, 1.16 ± 0.7. and 1.33 ± 0.4 for samples from air with < 20, $20 \cdot O_3 \cdot 50$, and > 50 ppbv O_3 respectively. These values are comparable to the ratio of TNMOC/· Speciated VOC's we measured in Azusa, California during September and October of 1997 of 1.3 ± 0.3.

Here we describe development of a new instrument to measure the airborne total non-methane organic carbon concentration (TNMOC), and the ratio of this value to the sum (·) of speciated VOC's measured by standard gas chromatography (GC-FID). The approach is to make an *in situ* measurement that minimizes sample contact, cryo-trapping whole air samples with minimal trapping of CO_2, CO and CH_4. Samples are processed by an oxidation catalyst to generate CO_2 that is measured as TNMOC. Alternatively, a standard speciated VOC's measurement is made with the same instrument. The TNMOC instrument described here has several improvements compared to previous approaches. Samples introduced into our instrument are exposed to only an inlet tube, valve and short length of transfer tubing, and then immediately analyzed. Water management is not needed. Speciated VOC's are measured with the same instrument, avoiding problems created by comparing different sample inlets and calibrations.

Instrument Description

The technique to make the TNMOC measurement centers on a cryogenic separation of reactive carbon from CO, CO_2 and CH_4. A schematic for the process is shown in Figure 1. In step 1, the first trap (trap I) is cooled to between -55 and -80 ûC. The sample passes through the sampling tube and a heated valve before passing through trap I. The target TNMOC condenses, while CH_4, CO, and most of the CO_2 pass through. Once the sampling (cryo-trapping) stage is finished, trap I is purged with helium (40 s at 16 mL/min) to remove sample gas from the tubing and air space within the trap. In step 2, trap I is rapidly heated; and a He/O_2 mix sweeps the desorbed TNMOC into an oxidation catalyst where the organics are converted to CO_2 (200 s at 16 mL/min). An advantage of this method is that decomposition or reaction of labile compounds during trapping and heating has no effect on the result, because the trapped organics are immediately oxidized to CO_2. The CO_2 is focused in trap II, which is immersed in lN_2, to concentrate the (~50 mL) volume necessary to thoroughly desorb the contents of trap I into a small plug for the quantification step. Finally the focusing trap is heated and the TNMOC, which has been converted to CO_2, flows into column I and is catalytically converted at the end of column 1 to CH_4 and quantified with an FID.

The TNMOC instrument is built around a dual FID GC (Hewlett Packard 5890-II). Inlet valves (Valco) are attached to an aluminum block maintained at 50-60 ûC. Transfer lines, trap tubing and fittings are constructed from deactivated fused silica lined stainless steel (Restek) and are maintained above ambient temperatures with heating tape. Temperature controllers (Omega) maintain heating and cooling of trap I, the methanation and oxidation catalysts and the valve block. Trap II is alternately cooled and heated by immersing it in liquid nitrogen and hot water. Both traps I and II are filled with silanized glass beads and are constructed of 1/4" and 1/8" outer diameter (OD) tubing, respectively. Trap I is cooled from the center with pulses of lN_2 vapor, so that there is a significant temperature gradient along the length of the tube. As a result, the trap's temperature, which is recorded by a thermocouple attached close to the center of the tube, is a relative value. Each time this trap is replaced, the trapping of CO_2 as a function of temperature is determined and a new optimal operational temperature is chosen, typically falling in the range -55 to -80 ûC. The oxidation and reduction catalysts are constructed of 1/8" OD stainless tubing packed with unsupported Pd (Aldrich), and Ru (Ann Arbor Specialty Chemicals) granules maintained at 700 and 300 ûC respectively. Mass flow controllers (Unit Instruments) provide stable flows of He, He/O, and sample flow.

One of the most interesting aspects of the TNMOC measurement is its comparison to the sum of the speciated VOC's as they are commonly measured. The ideal way to make this comparison is to acquire two identical samples simultaneously, and process one sample in

TNMOC mode and the other in speciated mode, with separate GC columns. Prior to the field measurements described below, we installed a second GC column and FID. After the field campaign, an identical sampler in parallel was added. The columns used for both TNMOC and Speciated measurements are 60m x 0.32mm ID x 1μm DB-1 (J&W). This column was chosen because the stationary phase (100% methyl polysiloxane) is among the most widely applied in field measurements of VOC's [1, 6-8]. Ideally, 100% of the NMOC in the air sample stays in trap I, and CO, CO_2, and CH_4 pass through. In practice, CO and CH_4 (boiling points (T_b) of -191.5 and -164 ûC, respectively) pass through, while CO_2, with an ambient concentration larger than the TNMOC by a factor of 100-40,000 and a sublimation point of -78.5 ûC, traps to a minor degree, while the C_2-C_4 hydrocarbons are not trapped. The TNMOC detection limit is determined not by the absolute amount of atmospheric CO_2 that traps but by its variability. We can achieve trapping of CO_2 equivalent to about 50 ± 10 ppbv in a 500 mL sample. The amount of CO_2 trapped is traded off, however, with the trapping of C_4-C_5 hydrocarbons. In the field, we chose conditions that trapped 300 ± 40 ppb of CO_2, thus our detection limit (~3 x the CO_2 noise level) was about 120 ppbC. The amount of trapped CO_2 is measured continually, and includes CO_2 background caused by the carrier gasses.
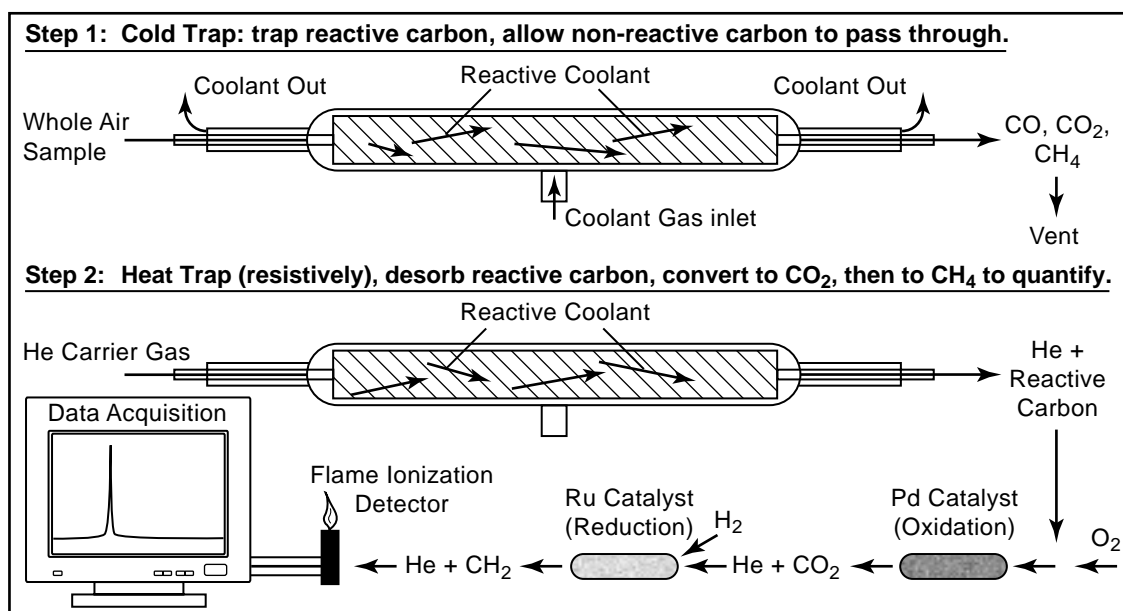

Figure 1. Process schematic of the approach for the TNMOC measurement.

The TNMOC instrument can be operated in three modes: 1) *TNMOC*: The sample is oxidized over a Pd-catalyst to CO_2, run on column 1 and analyzed with FID after conversion to methane over Ru. 2) *Speciation, column 1*: No oxidation, column 1, Ru methanizer and FID. This mode was necessary to establish the amount of CO_2 captured in trap I to order to correct TNMOC measurements. This mode is not ideal for speciated VOC's due to losses of heavy hydrocarbons in the methanizer. 3) *Speciated VOC's:* No oxidation, column 2 analyzed with FID (no methanizer). This is the standard speciated hydrocarbon analysis. TNMOC (mode 1) and Σ Speciated VOC's (mode 3) chromatograms of ambient air acquired in Azusa, CA are shown in Figure 2.

Field Measurements at Azusa, CA during September and October 1997

Field measurements were carried out at the SCAQMD's Azusa Station from September 4 to October 10, 1997, as part of the Southern California Oxidants Study (SCOS-97). The Azusa

site has been a PAMS site since 1994, and is located at the foot of the San Gabriel Mountains downwind of Los Angeles near the intersection of the 210 and 605 freeways in a mixed residential and light industrial area. The site experiences significant local sources of VOC's, and typically experiences some of the highest O_3 levels in the heavily populated portions of the Los Angeles air basin. The summer of 1997 had, however, the cleanest air on record.

For this campaign, the sampling line was constructed from 9.7 m of 1/8" Silcosteel tubing (Restek) with an inlet about 2.5 m above the roof. The three meters inside the heavily air-conditioned station were wrapped with heating tape and maintained at about 50 $^{\circ}$C to prevent condensation of water in the sampling line. Flow through the sampling line was maintained at 1 L/m with a diaphragm pump, and the sample was drawn through a tee at 20 or 50 mL/min. The residence time in the sampling line was about 4 s. The identification of the peaks discussed below is based on reference chromatograms constructed using samples from an EPA PAMS 59 compound retention time standard cylinder provided by the SCAQMD. These chromatograms were taken under dry and CO_2-free conditions, so the Azusa retention times were adjusted by using the most clearly identifiable peaks as markers. Retention times were checked against measurements made by the co-located EPA GCMS instrument, which uses the same type of column phase. The identification of methanol, acetaldehyde, ethanol, α-pinene, limonene, and several other species is based on the EPA GC/MS-instrument. All identities, but particularly the oxygenates and biogenics, should be considered tentative.
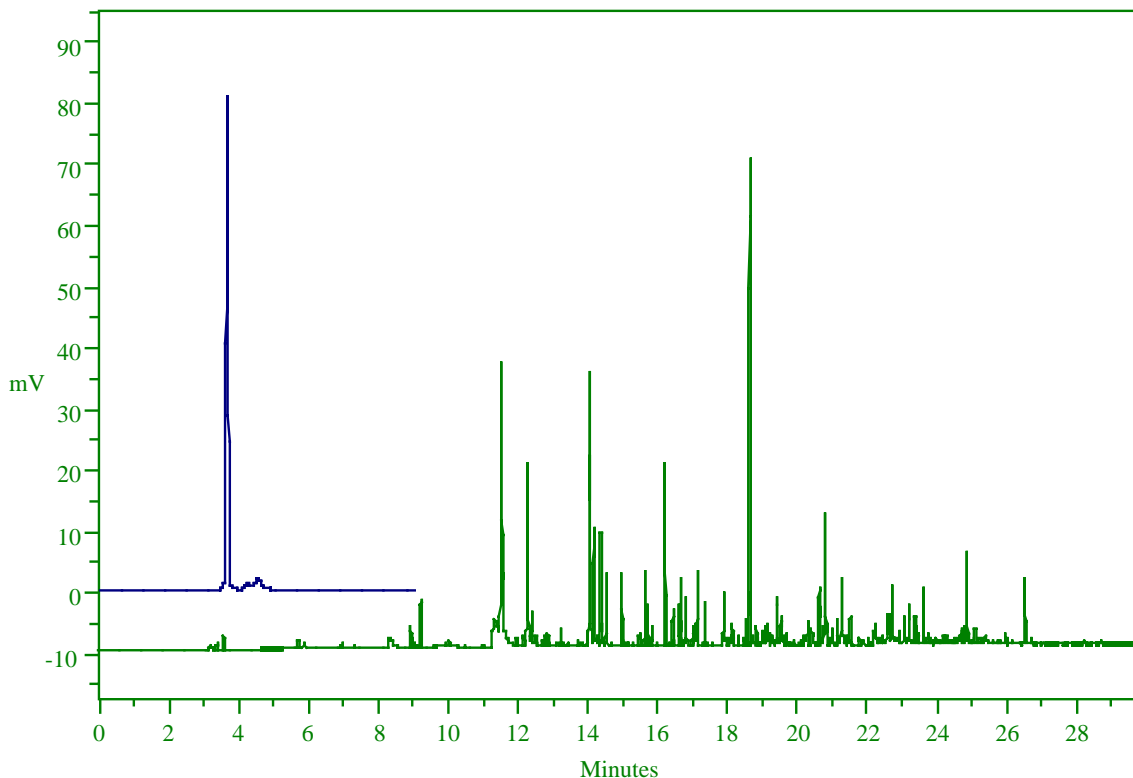

Figure 2. Sample chromatograms acquired 9/19/97 10:30 -11:00 AM at the Azusa station . Upper chromatogram, TNMOC, 550 ppbC. The lower chromatogram, Speciated VOC's, 460 ppbC has been multiplied by 6.5 and shifted down with respect to the vertical axis by 10 mv . Each sample was 500 mL.

Ten calibrations with a 1.08 ppmv n-hexane standard were performed at Azusa, resulting in uncertainty ± 2 and 3 % for the TNMOC and Speciated VOC's channels, respectively (1 σ). The variability in the trapped ambient CO_2 was ± 40 ppbC, or ± 8 % (1 σ). This variability no doubt contributes to the scatter in TNMOC measurements, although it is a small fraction of the observed scatter in the TNMOC measurements, the majority of which is presumably due to airmass variability. TNMOC and speciated VOC's measurements were made sequentially during the Azusa campaign, using two different protocols: (1) One sample/hour, alternating TNMOC and Speciated VOC measurements, 800 mL at 20 mL/min, first 19 of 84 samples, and (2) Two samples/hour, alternating TNMOC and Speciated VOC's, 500 mL at 50 mL/min, remaining 65 samples. The sample frequency is limited by the 35-40 minutes needed for chromatography of the Speciated VOC's. The TNMOC measurement (10 minute chromatogram) was made first, because this allowed the two samples to be collected as close together as possible (15-20 minutes).

Measurements and Comparisons of TNMOC and Speciated VOC's

Measurements of TNMOC are plotted vs. time of day in Figure 3. TNMOC averaged 530 ± 200 ppb (1 σ) with a weakly decreasing trend over the course of the day, and high variability in the morning hours. The · Speciated VOC's data has a similar trend with an average concentration of 410 ± 150 ppbC (1 σ).
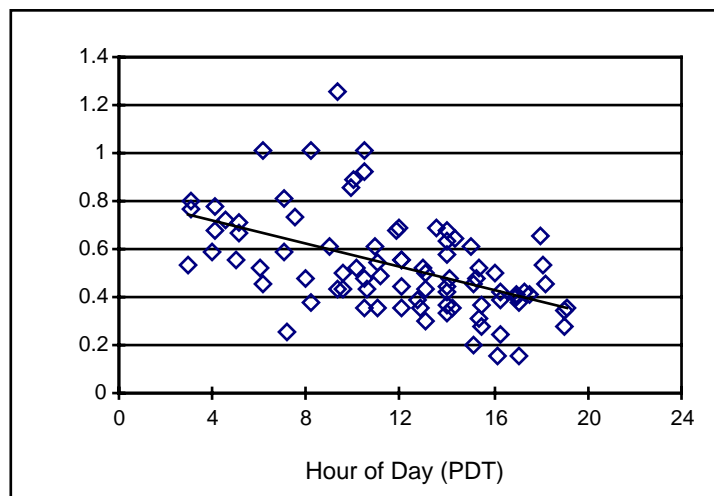

Figure 3. TNMOC (ppmC) vs. Hour of day. The line indicates a linear correlation with the equation y = -0.024x +0.8, and has an R value of 0.51. The average TNMOC concentration was 520 ppbC.

One of the primary goals of the TNMOC instrument is to determine the amount of organic carbon in ambient air that is not detected in conventional GC analysis. The ratio of TNMOC/Speciated VOC's for 83 pairs of measurements made between Sept. 4 and Oct. 10 are plotted versus time of day in Figure 4. The average T/S ratio is 1.29 ± 0.27 (1 σ). The scatter in the data is large, but the deviation of this value from 1 is highly significant; the 95% (2 σ) confidence interval for the mean value is ± 0.07. A ratio greater than 1 indicates that in conventional VOC measurements using GC analysis underestimates the amount of TNMOC.

Contribution of Light Oxygenates to the Excess TNMOC

A candidate for the source of the excess TNMOC compared to the · Speciated VOC's observed in Azusa is the oxygenated VOC's that are detectable with GC-FID but have reduced responses relative to hydrocarbons due to their heteroatom content [Jorgensen, 1990 #335], and thus contribute less to the · Speciated VOC's than to TNMOC. Most oxygenates were not quantifiable in our speciated chromatograms, but we could estimate the concentrations of methanol, ethanol and acetaldehyde. Methanol averaged 6 ppbC or about 1.3% of the total carbon, and acetaldehyde and ethanol each contributed about 2% to the TNMOC. The average acetaldehyde concentration was 8.4 ppbC, in agreement with 6 ppbv measured at Azusa in 1993 [9]. Ethanol averaged 11 ppbC. Roughly half of the carbon in the methanol, ethanol and acetaldehyde is already accounted for in the Σ Speciated VOC's measurement (FID responses are equivalent to 0.77, 1.65 and 1.02, respectively, [10]). These three compounds sum to about 5% of the total VOC loading, 2-3% of which is already included in the · Speciated VOC's. Thus these three common oxygenates can account for 10% or less of the difference between TNMOC and the · Speciated VOC's.
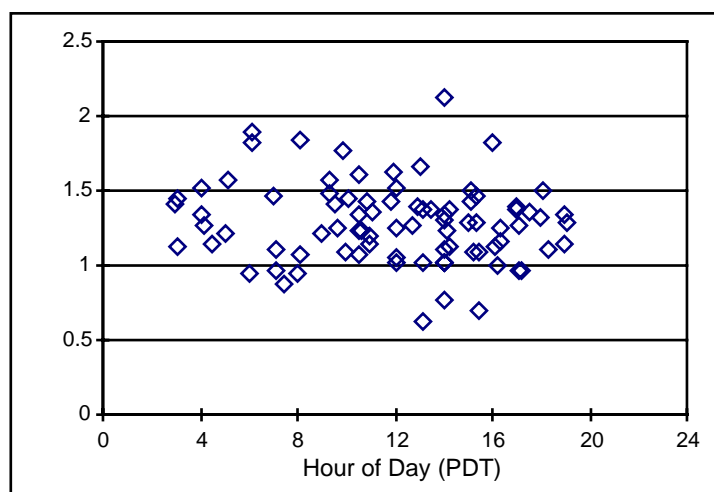

Figure 4. Ratio of TNMOC to · Speciated VOC's as a function of time of day. The average TNMOC/· Speciated VOC's was 1.29 ± 0.27

Hydrocarbon Age/Photochemical Processing

Another potential source of the 30% excess TNMOC over speciated are the multi-functional species similar to those generated in the isoprene and *m*-xylene chamber experiments described above. Azusa normally experiences quite polluted air during the "smog season" (July to October), but 1997 was the cleanest year on record, and our data set contains O_3 levels 95% of which were at or below 70 ppbv and 60% at or below 40 ppb. To estimate the extent of photochemical processing of hydrocarbons arriving at the Azusa station, ratios for several pairs of aromatic hydrocarbons from the speciated VOC chromatograms were calculated [11, 12]. Ignoring the effect of dilution, the ratio of two hydrocarbons should evolve according to the following equation:

$$\ell n \frac{[A]}{[B]} = \ell n \frac{[A]_0}{[B]_0} - \left(k_A - k_B\right)[OH]t \qquad \text{(E 1)}$$

where [X] and $[X]_0$ are the species concentrations at the time of the measurement and in the source, respectively, k_x is the rate constant for reaction of X with OH radicals and [OH] is the average OH concentration during the time period t. Here we focus on the m&p-

xylene/ethylbenzene ratio, since these compounds are highly correlated and the peaks could be reliably quantified. m- And p-xylene are not separated by a DB-1 column, thus their concentration is combined. The primary sources of these three aromatics are unburned or evaporated fuel [13]. Rate constants for reaction ethylbenzene and m&p-xylene with OH of 0.71, 2.2 and 1.4 x 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively were assumed [14, 15].

At night our m&p-xylene/ethylbenzene ratio had a value of 3.8 - 3.9 (Figure 5) in excellent agreement with the value reported for Los Angeles gasoline in 1975 [13] and ambient air in 1987 [12]. The magnitude of the decrease during the day is presumably an indicator of the level of photochemical activity. Indeed, the inverse correlation between the m&p-xylene/ ethylbenzene ratio and O$_3$ has an R value of 0.77. From the decrease of the ratio ln (m&p-xylene /ethylbenzene) from 1.35 at night to between 0.8 and 1.0 in the afternoon, an average exposure to OH can be calculated from (E1), and corresponds to 1.8 hours of exposure 0.2 ppt of OH.

With this estimate of hydrocarbon processing, a calculation of the expected degree of increased oxygenation/nitration of the organics can be made relying on the following assumptions: 1) the average speciated mixture of 100 hydrocarbons from the EPA for 29 cities at 6-9 AM survey [16], 2) rate constants for each hydrocarbon reacting with OH, and for alkenes with ozone, 3) exposure to 0.2 ppt OH and 50 ppbv O$_3$ for 1.8 hours, and 4) equation (E2):

$$[A]=[A]_0 e^{-\left(k_A[OH]+k_{O3}[O_3]\right)t}$$

(E 2)

Under these conditions, an average of 27% of the hydrocarbons react once with either OH or ozone. Since the organics have an average of 7 carbons [16], and can be expected to add ~1.5 functional groups (primarily alcohol, carbonyl, or nitrate) per reaction, the total mix might increase its heteroatom content relative to the carbon by about 6%. The effect of this modest increase on the TNMOC/· Speciated VOC's ratio cannot be calculated precisely since the effect of oxygenation/nitration can be to either reduce the FID response or to cause the compound to be lost or broadened in the column so as not to be quantifiable. The latter reduces the sum of speciated VOC's more than the former. It is clear, however, that given the low level of photochemical processing in this data set, the T/S ratio could be expected to have relatively little dependence on the time of day (Figure 3), ozone level, or the ratio of m&p-xylene/ethylbenzene (not shown). Indeed, no trends are observed; each relationship has a correlation coefficient of less than 0.05.
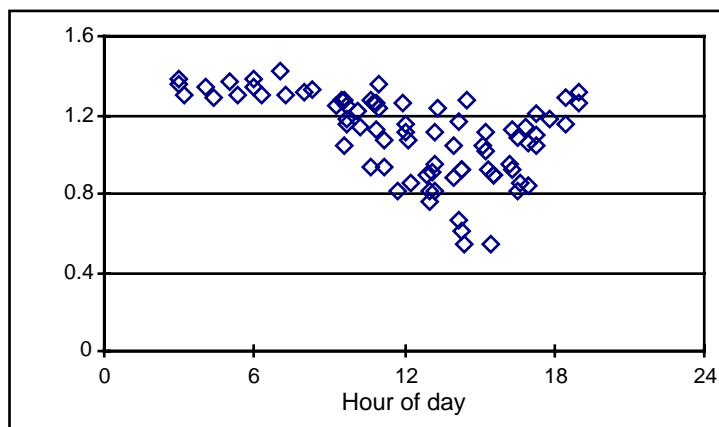

Figure 5. ln(m&p-xylene / ethylbenzene) versus hour of day.

Conclusions

The results from the field campaign in Azusa, CA are surprising, showing that even in air with minimal photochemical processing, the ratio of the TNMOC to the sum of speciated VOC's is 1.3 ± 0.3. The source of this difference, as well as its spatial and temporal variability remains to be determined. About 10% of it is from the light oxygenates methanol, ethanol and acetaldehyde, which are only partially measured by an FID. A contribution from directly emitted semi-volatile heavy hydrocarbons is possible [1, 17, 18]. The difference in the Azusa data set is probably not due to large quantities of heteroatom containing oxidation products reaching the station, since the air during most of the late summer of 1997 was unusually clean; the maximum level of oxygenation/nitration due to photochemistry was less than 10%. The variability is due to a combination of short term variability in both local sources and in air mass history and highlights the requirement that TNMOC and sum of speciated VOC's to be made in parallel, preferably by the same instrument. Clearly, these initial results are intriguing and further investigation is warranted.

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