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# AMBIENT VOC MEASUREMENTS IN MEXICO CITY DURING THE MCMA 2002 & 2003 FIELD CAMPAIGNS

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## 1. INTRODUCTION

The Mexico City Metropolitan Area (MCMA) represents one of the largest and most polluted cities on the globe. Recent changes have been implemented to reduce elevated pollution levels and some improvements in particulate levels and lead levels have been documented (Molina and Molina, 2002; SEMARNAT et al., 2002), but levels of fine particulate, ozone, and a variety of air toxics remain among the highest in the world. The location of the MCMA in a deep mountain basin at a high elevation (2240 m.a.s.l.) and subject to frequent inversions, the density and magnitude of the population (more than 18 million inhabitants), and the motivation to improve the standard of living in the MCMA all combine to produce substantial challenges to further improvements in MCMA air quality. To help guide future control efforts, a comprehensive assessment of air quality in Mexico City has been undertaken (Molina and Molina, 2002). A key piece of this assessment was the performance of a field campaign MCMA 2003 that emphasized the combination of a wide variety of state-of-the-art instrumentation and methods

The MCMA 2003 field campaign was a comprehensive investigation of photochemical gas and aerosol air quality in the Mexico City megacity conducted during April 2003. A preliminary study was also conducted during February 2002. As part of both studies, ambient VOC samples were collected from airshed boundary sites, central urban core sites and downwind urban receptor sites. Samples were also obtained during mobile vehicle chase operations designed to obtain data on direct vehicle emissions. In this paper, preliminary results from the VOC measurements are presented in terms of the distribution of VOC species and the magnitudes and diurnal patterns of VOC levels. The use of ratios of individual VOC species are used to characterize different sites, to investigate the relative reactivity of different species, and for comparison to similar analyses conducted in the United States. VOC ambient distributions are also compared to distributions in the available emission inventory for Mexico City.

## 2. EXPERIMENTAL METHODS

VOC ambient concentrations were measured using a combination of methods including: 1) fixed site whole air canister sampling, 2) continuous real-time olefin detection with a chemiluminscent olefin detector, 3) mobile conditional canister sampling of vehicle exhaust and GC/FID analysis, and 4) real-time, continuous VOC measurements using a Proton Transfer Reaction Mass Spectrometer (PTR-MS) onboard the mobile laboratory and a second PTR-MS operated at a tall urban tower. During selected periods, the mobile laboratory was employed as a fixed site monitoring station, while at other times, the mobile system was used in a vehicle chase mode to measure fresh mobile emissions. In addition to these measurements, other investigators operated open path spectroscopic instruments that were sensitive to an array of VOCs (see Grutter, 2003, for example). Results from these other optical systems are not included in this preliminary presentation of VOC data.

In both campaigns, VOC samples were collected at several fixed sites within and on the boundary of MCMA. Key sites included:
1) Cenica lab rooftop in southeastern MCMA 2) La Merced, a central urban monitoring site, and 3) Pedregal, a residential monitoring site that is in the prevailing downwind direction from central Mexico City. Whole air samples were collected in either one liter or six liter electropolished stainless steel

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canisters. Fixed site samples were collected with usually a three hour averaging interval, while conditional samples collected in the mobile laboratory were obtained in a semi-automated operation dependent upon observed CO2 concentrations. CO2 was used as a tracer for the vehicle exhaust plume. With high CO2 levels, air was drawn into a 'chase' canister, and during low CO2 levels, air was drawn into a 'urban background' sample. Approximately half of all of the canister samples were analyzed at a field laboratory in Mexico City and the remainder were returned to WSU for analysis. In both cases, samples were analyzed using cryogenic pre-concentration with temperature programming on a gas chromatograph with flame ionization detection.

The real-time chemiluminescent olefin detector was originally developed as a fast isoprene sensor (FIS, Guenther and Hills, 1998). However, in an urban environment, the instrument responds, with varying sensitivity, to a variety of olefins. For the MCMA 2003 study, the FIS was employed as an olefin eddy covariance flux instrument and operated at a tall urban tower in conjunction with a 3-d sonic anemometer and a PTR-MS. A 27 m tower was installed on the roof of the 10 m tall Cenica laboratory building in southeastern Mexico City. Air was drawn from 37 m above ground through Teflon tubing to the instruments housed in a shelter on the roof of the building. The FIS was operated continuously and the data were recorded at 10 Hz. At various times, whole air samples were also collected through the tower sample line. In this paper, ambient olefin concentrations are reported for this system. Flux data will be presented elsewhere.

The PTR-MS systems were operated by Montana State University (MSU) onboard the mobile lab and by Pacific Northwest National Laboratory (PNNL) at the urban tower site. The PTR-MS is a sensitive real-time detector for selected VOCs. It can be operated in a scan mode to detect a wide range of VOCs or in selected ion mode to monitor specific VOC ions (Lindinger et al., 1998).

Emission inventories for MCMA have been developed and employed for gridded photochemical modeling (Molina and Molina, 2002; Jazcilevich et al., 2003). As such the inventory includes some classification of VOC types, but not at the same level of detail as obtained with the VOC whole air analysis system. Further, initial modeling efforts included adjustment of the VOC total emissions by a factor of three (3X VOC) in order to obtain acceptable levels of performance for urban ozone simulations. Although an improved inventory is under development, we employ the unadjusted gridded inventory for comparison purposes in this paper.

## 3. PRESENTATION OF RESULTS

The ranked median concentrations of individual VOCs for 6 to 9 am from the 2002 campaign are summarized in Table 1 (next page). Results are included from Parrish et al. (1998) for median VOC concentrations from 39 U.S. cities. These data show the disproportionate amount of alkanes that occur in Mexico City compared to the U.S. The elevated levels of light alkanes are attributable mainly to the widespread use of liquefied petroleum gas for water heating and cooking in Mexico City. The results also show that ambient levels of many, but not all, of the VOCs are higher in Mexico compared to the US median. The median of the ratio of Mexico to US VOCs is 1.4 and the ratio of the total VOCs in Mexico to US total VOCs is 2.4. The latter number is influenced by the large concentrations of propane and other light alkanes.

The distribution of VOCs in Mexico City can also be compared on the basis of reactivity with OH radical to the distribution in the US. As shown in Figure 1, the reactivity of MCMA VOCs is higher in all but three cases compared to the median US results. The elevated levels of propane and butane are sufficient to rank these alkanes in the top five in reactivity in MCMA, while their ranking in the US data set is much lower.

The median ambient data are lumped into the inventory modeling classes in Table 2. For comparison, the total emissions by each class (prior to the 3X correction used for modeling) are also included in the table along with the corresponding percentage of the total. This comparison of early morning ambient data and gridded total emissions suggests that the inventory underestimates the contribution of ALK1, PROPANE, ARO2, ARO1 and C2 hydrocarbons. It is possible to use the ambient data as a guide for how much the inventory might need to be adjusted by class to yield the same distribution of VOCs as observed in the ambient data. The resulting adjustment factor, which takes into account the molecular weight of each class, is shown in the last column in Table 2. These results show that the inventory for some of the classes

Table 1. Median 6-9 am VOC concentrations (ppbv).

| Compound | Mexico 2002 | US urban 39 cities | Ratio |
|---|---|---|---|
| propane | 335.8 | 23.5 | 14.2 |
| n-butane | 150.7 | 40.3 | 3.7 |
| toluene | 68.9 | 33.8 | 2.0 |
| i-butane | 60.0 | 14.8 | 4.1 |
| i-pentane | 58.3 | 45.3 | 1.3 |
| C2's | 44.1 | 57.6 | 0.8 |
| m,p-xylene | 32.5 | 18.1 | 1.8 |
| 2,2,4-trimethylpentane | 21.3 | 6.8 | 3.1 |
| 2-methylpentane | 21.1 | 14.9 | 1.4 |
| 2,3-dimethylbutane | 19.5 | 3.8 | 5.1 |
| n-pentane | 18.9 | 22.0 | 0.9 |
| 1,2,4-trimethylbenzene | 18.3 | 10.6 | 1.7 |
| o-xylene | 13.5 | 7.2 | 1.9 |
| Benzene | 12.2 | 12.6 | 1.0 |
| 3-methylpentane | 12.1 | 10.7 | 1.1 |
| Hexane | 11.9 | 11.0 | 1.1 |
| Propylene | 11.0 | 7.7 | 1.4 |
| Ethylbenzene | 10.0 | 5.9 | 1.7 |
| i-butene | 9.6 | 5.9 | 1.6 |
| 2,3,4-trimethylpentane | 9.3 | 2.5 | 3.7 |
| Methylcyclopentane | 9.1 | 6.4 | 1.4 |
| 3-methylhexane | 8.2 | 5.9 | 1.4 |
| p-propylbenzene | 8.2 | | |
| MTBE | 6.8 | | |
| 2,2-dimethylbutane | 6.4 | | |
| o-ethyltoluene | 6.2 | 2.9 | 2.1 |
| Cyclohexane | 5.9 | 2.2 | 2.7 |
| n-heptane | 5.5 | 4.7 | 1.2 |
| 1,3,5-trimethylbenzene | 5.4 | 3.0 | 1.8 |
| n-octane | 4.3 | 2.6 | 1.7 |
| 2-methylhexane | 4.2 | 7.3 | 0.6 |
| 2,3-dimethylpentane | 3.6 | | |
| Styrene | 3.3 | | |
| n-propylbenzene | 3.2 | | |
| m-propylbenzene | 2.4 | | |
| t-2-butene | 2.4 | 2.5 | 1.0 |
| Methylcyclohexane | 2.3 | 3.4 | 0.7 |
| c-2-butene | 2.1 | | |
| 2-methylheptane | 2.1 | 2.5 | 0.8 |
| 1,2,4 trimethyl cyclohexane | 1.9 | | |
| t-2-pentene | 1.8 | 2.9 | 0.6 |
| 1-pentene | 1.7 | | |
| 2-methyl-1-butene | 1.5 | 2.6 | 0.6 |
| 2-methyl-2-butene | 1.4 | | |
| c-2-pentene | 1.4 | 3.6 | 0.4 |
| 1-hexene | 1.2 | | |
| Propyne | 1.2 | | |
| 1,3-butadiene | 1.1 | | |
| Isoprene | 0.9 | | |
| Total | 1040.0 | 439.5 | 2.4 |
| total identified | 873.8 | | |
| % identified | 83.5 | | |

Table 2. Comparison of ambient VOC distribution & gridded modeling inventory VOC distribution.

| Model Species | NMHC median 6-9 am (ppbC) | % of total | Inventory $10^3$ tons/yr | % of invent. | Invent Adj. |
|---|---|---|---|---|---|
| ALK1 | 380.1 | 36.4 | 36.2 | 11.1 | 2.6 |
| PROPANE | 335.8 | 32.2 | 78.3 | 15.4 | 5.3 |
| ARO2 | 96.4 | 9.2 | 40.1 | 13.1 | 2.8 |
| ARO1 | 72.1 | 6.9 | 42.8 | 12.3 | 3.1 |
| ALK2 | 58.8 | 5.6 | 15.8 | 24.0 | 1.0 |
| C2 | 44.1 | 4.2 | 22.9 | 3.4 | 1.6 |
| OLE1 | 24.7 | 2.4 | 7.8 | 4.8 | 0.6 |
| BENZENE | 12.2 | 1.2 | 8.6 | 2.6 | 0.7 |
| OLE2 | 11.5 | 1.1 | 11.2 | 7.0 | 0.8 |
| MTBE | 6.8 | 0.6 | 50.1 | 3.9 | 3.4 |
| BUTD | 1.1 | 0.1 | 0.0 | 0.0 | 0.0 |
| ISOP | 0.9 | 0.1 | 12.7 | 2.4 | 0.9 |
| | 1044.5 | 100.0 | 326.5 | 100.0 | 23.0 |

might need to be adjusted upward by factors of 2 to 3 or more, but that not all classes are necessarily overestimated. Of course, this is a relatively simple approach that does not fully account for the spatial and temporal distribution of emissions, the small number of monitoring sites, or for any early morning chemistry that might affect the ambient levels.

Parrish et al. (1998) have outlined a very useful approach for examining VOC ambient data that involves examination of ratios of specific compounds. For relatively unreactive compounds such as I-butane and n-butane, the effects of ambient dilution are shown in a graph of I-butane concentration versus n-butane concentration (see Figure 2a). We have the advantage of being able to include vehicle chase samples that represent very fresh emissions. The slope of the line through the chase samples can be used as a guide for determining when one of the compounds is affected by other sources or by chemistry. This is illustrated in Figure 2b in terms of ethylbenzene which is more reactive than toluene. For sites where significant chemical processing has occurred, the ethylbenzen/toluene ratio decreases compared to the ratio from fresh emission samples. In contrast, Figure 2c shows the effects of nearby sources of toluene compared to benzene. In this case, data from some of the sites falls along the dilution line, but at the Xalastoc site, toluene levels were elevated compared to dilution of mobile emissions. This is attributable to the fact that the Xalastoc site was at an automobile dealership that included a vehicle paint shop.

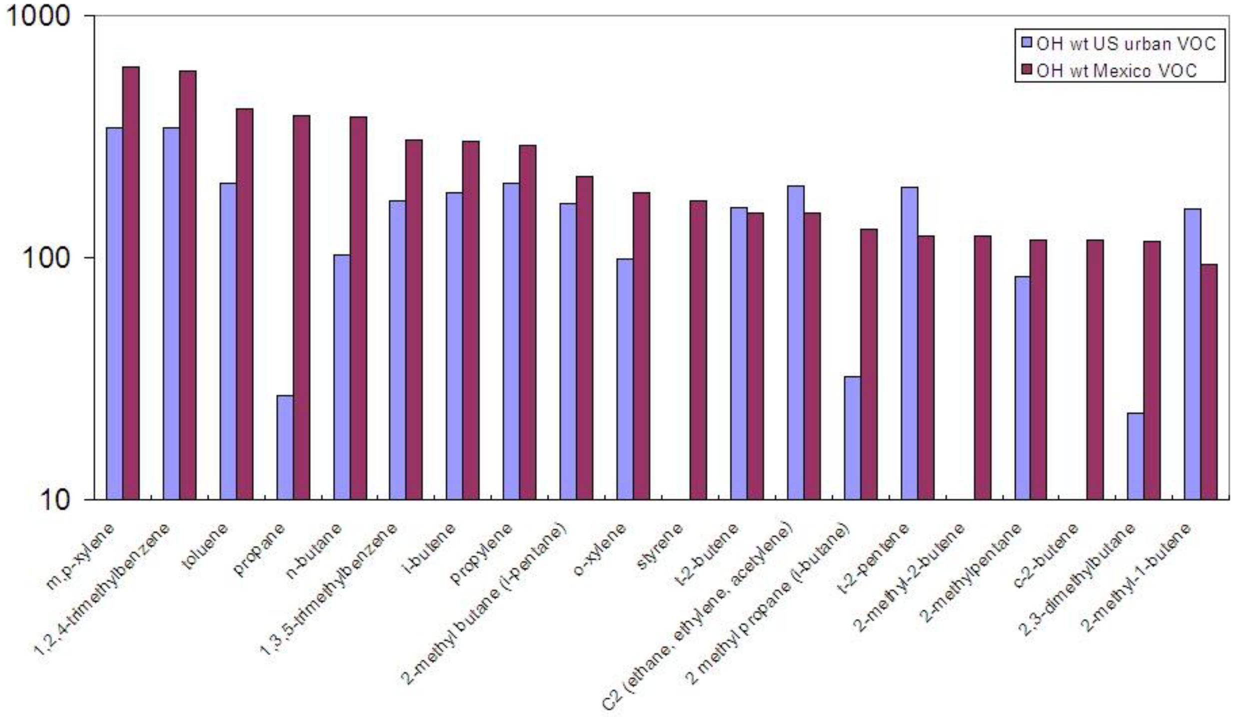

Figure 1. Distribution of relative VOC reactivity weighted by the OH reaction rate for Mexico City and the median levels for 39 US cities.

In addition to canister sampling, VOC measurements were also obtained in 2002 and 2003 using PTR-MS instruments on the mobile laboratory and at the urban tower. In 2002, we compared the response of the PTR-MS with canister VOC data and found very good agreement for some species, including benzene, toluene, C2-benzenes and C3-benzenes (Figure 3). There was poor agreement for styrene and C5 alkenes. The PTR-MS has a significant advantage in detection of oxygenated VOC compared to canister methods. The combination of methods suggests that oxygenated VOCs contribute an additional 20% not identified by canister sampling to the overall VOC burden as shown in Figure 4.

The FIS olefin detector provides another method to obtain continuous VOC concentration measurements. As shown in Figure 5, the diurnal average profile of olefins measured from the urban tower exhibits a clear early morning traffic signal. The difficulty in using the FIS data is to determine what the FIS response represents. Guenther and Hills (1998) presented FIS response factors for a number of compounds. According to their data, the FIS response (relative to isoprene) is 1 for propene and has a decreasing sensitivity for other olefins. We can compare the FIS signal to the sum of olefins as measured with the canister sampling system. Data shown in Figure 6 suggest that generally the FIS response provides an upper bound on the identified olefins. Except for one early morning sample period when the FIS response was significantly larger than the canister result, the FIS signal shows relatively good agreement with the canister data.

## 4. SUMMARY

A number of different methods were used to measure VOC concentrations in Mexico City during the MCMA 2002 and 2003 field campaigns. The data are consistent with previous measurements that show significantly higher levels of light alkanes compared to US cities (Mugica et al., 2003; Vega et al., 2000; Arriaga et al., 1997). The levels of most other VOCs are also elevated compared to the median for US cities. Examination of the VOC data in terms of lumped modeling VOC classes and comparison to the gridded emission inventory suggests that some classes are underestimated in the inventory by factors of 2 to 3. The use of ratios of individual VOCs is useful for examining the effects of chemistry or nearby sources on measured VOC

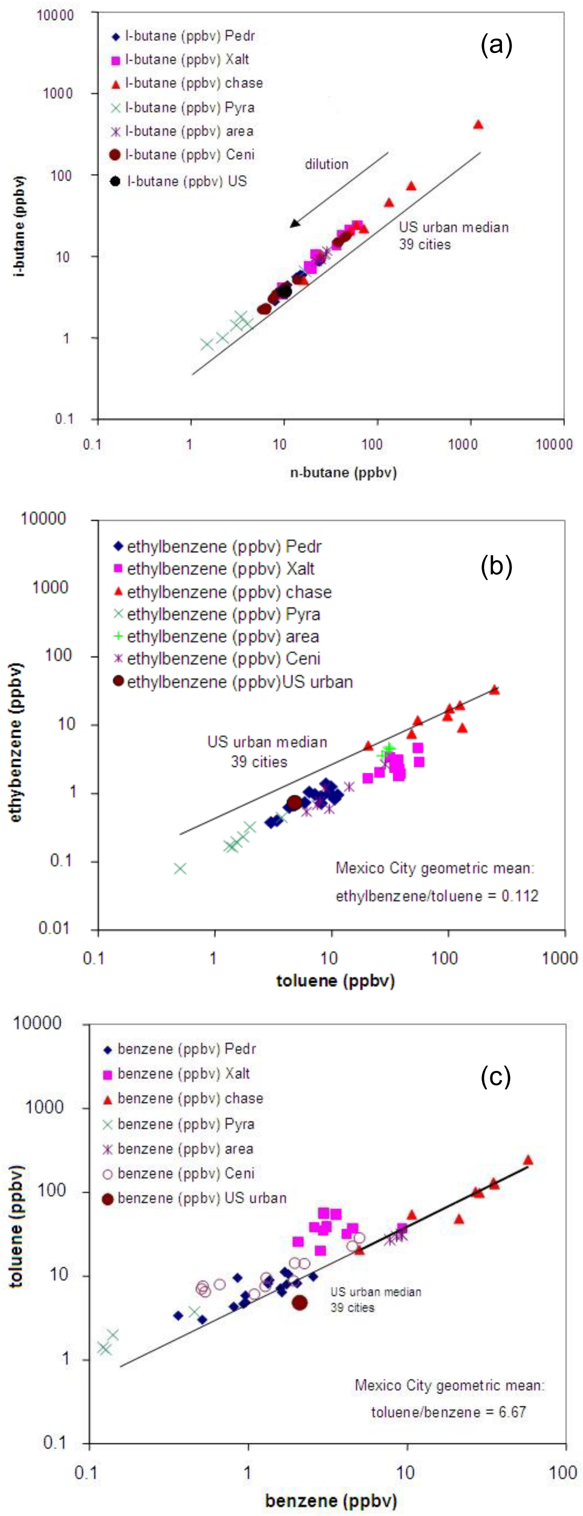

Figure 2. a) I-butane versus n-butane for MCMA 2002 samples b) Ethylbenzene vs toluene for MCMA 2002 samples and c) toluene vs benzene for MCMA 2002 samples and the median value for 39 US cities (Parrish et al., 1998).

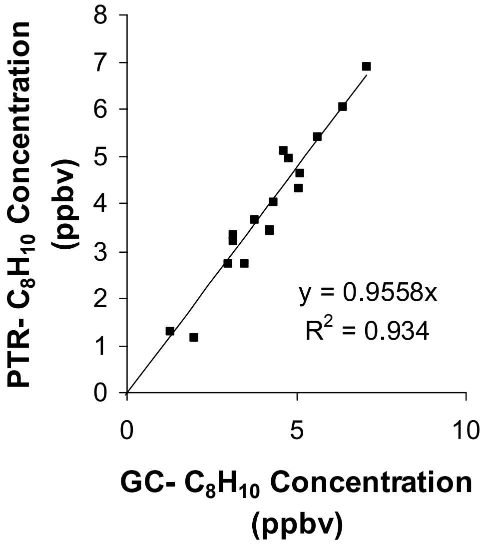

Figure 3. Comparison of PTR-MS response to C2 benzenes and GC/FID canister data for C2 benzenes.

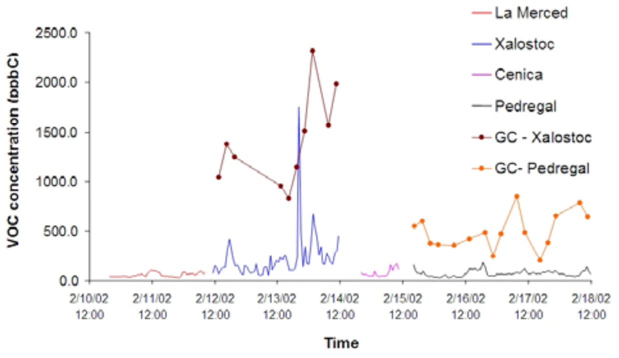

Figure 4. Total identified VOC from GC/FID canister sampling and corresponding identified oxygenated VOC from PTR-MS monitoring.

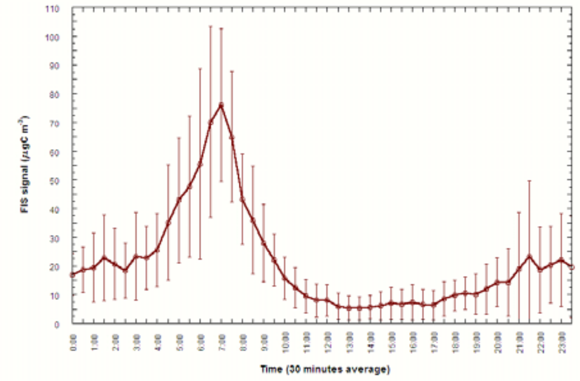

Figure 5. Diurnal average olefin concentration (as propene) measured with the FIS from the urban tower during April, 2003.

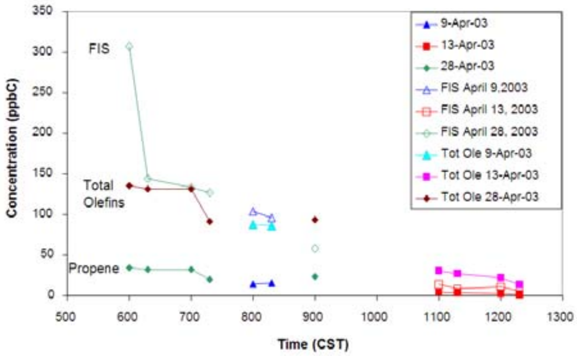

Figure 6. Comparison of identified olefins from GC/FID measurements with FIS olefin measurements during April, 2003.

levels. Comparison of PTR-MS results with GC/FID data showed very good agreement for a number of aromatics, and the PTR-MS data for oxygenated VOC suggests that oxygenated VOC contribute an additional 20% to the overall VOC burden. The use of the FIS isoprene instrument as an urban olefin detector provides another way to obtain continuous VOC data. The diurnal olefin profile shows an early morning traffic response.

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