JP1.11

AMBIENT VOC MEASUREMENTS IN MEXICO CITY

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1. INTRODUCTION

Volatile organic compounds (VOC) are a key piece in understanding photochemical air quality in urban atmospheres. In the presence of sunlight and nitrogen oxides (NO_x), VOC are oxidized to carbon dioxide and water via various intermediates: radicals (e.g., hydroxyl, hydroperoxy, organic peroxy), oxygentated organics (e.g., aldehydes, acids, alcohols, nitrates, peroxides), and inorganics (e.g., carbon monoxide, ozone, hydrogen peroxide, nitric acid). A number of VOC are also identified as toxic air pollutants and may have significant direct health impacts in urban areas. Measurements of VOC are thus necessary for future control efforts to improve the standard of life of millions of people living in extremely polluted cities, such as the Mexico City Metropolitan Area (MCMA). In the MCMA in the last decade, important changes have been implemented to improve air quality. Even with these changes, the pollutant levels remain among the highest in the world.

In this context, a comprehensive investigation of photochemical gas and aerosol air quality in the MCMA was 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. This paper presents a summary of the preliminary results from the VOC measurements 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.

The objectives of the VOC measurements include: 1) compare results from independent methods to provide confidence in the data and to identify areas of uncertainty, 2) obtain detailed ambient concentration data to improve our understanding of atmospheric photochemistry, 3) conduct direct and indirect source measurements to evaluate and improve emission inventory models, 4) employ ambient VOC and NO_X data to evaluate and improve photochemical models.

2. EXPERIMENTAL METHODS

VOC ambient concentrations were measured using a combination of methods including: 1) fixed site whole air canister sampling and GC/FID analysis, 2) continuous real-time olefin detection with a fast olefin sensor (FOS), 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.

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In both campaigns, VOC samples were collected at several fixed sites within and on the boundary of MCMA. Key sites included: 1) the CENICA supersite located in a densely populated section of 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 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 CO_2 concentrations. With high CO_2 levels, air was drawn into a 'chase' canister, and during low CO_2 levels, air was drawn into an 'urban background' sample. Approximately half of all of the canister samples were analyzed at a field laboratory in Mexico City and the remainders 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 FOS is a Fast Isoprene Sensor (FIS) (Guenther and Hills, 1998) calibrated with propylene instead of isoprene. Detection is based on chemiluminescent reaction between alkenes and ozone, and the detector responds with different sensitivity to a variety of olefins. Also there are reactions between ozone and other trace gases that could be potential interferences. In a preliminary test we found that the FOS has a more sensitive response to 1-3 butadiene and isoprene than to propylene, however, their ambient concentrations are low enough to produce a small signal compared to propylene. In comparison, species with a lower response than propylene, but with high concentrations in urban atmospheres (e.g. ethylene) can produce large signals. Thus, the FOS measures a mix of VOC responding as propylene and can be used to providing continuous, fast reponse measure of the levels of the olefinic mix of VOC in an urban atmosphere. During the MCMA 2003 study, the FOS was operated in an eddy covariance flux mode at a tall urban tower in conjunction with a 3D sonic anemometer. A 27 m tower was installed on the roof of a 10 m tall 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 FOS 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.

The PTR-MS systems were operated by Montana State University (MSU) onboard a 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 VOC. It can be operated in a scan mode to detect a wide range of VOC or in selected ion mode to monitor specific VOC ions (Lindinger *et al*., 1998) or in a selected scan mode (fewer masses) in a disjunct eddy covariance flux mode. Both modes were used in the MCMA campaign.

3. PRELIMINARY RESULTS

Results from canister sampling during the early morning rush hour provide a description of the distribution of VOC species that contribute to photochemical ozone and haze production. The median distribution of the 24 most prevalent VOC is summarized in Table 1. This distribution is compared to the median reported for measurements in a large number of U.S. cities (Parrish *et al*., 1998). The ratio of median concentrations between the MCMA measurements and US measurements show the abundance of alkanes in Mexico City compared to the US. The elevated levels of low molecular weight alkanes are attributable mainly to the widespread use of liquefied petroleum gas for water heating and cooking in Mexico City. The levels of toluene in Mexico City also appear to be higher than in the U.S. The median of the ratio of Mexico to US VOC is 1.6 and the ratio of the total VOC in Mexico to US total VOC is 2.7. The latter number is influenced by the large concentrations of propane and other light alkanes.

The distribution of VOC 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 VOC 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.

These results can also be compared to the distribution of VOC classes represented in current emission inventory (EI) developed for Eulerian grid modeling. The median ambient data are lumped into the inventory modeling classes in Table 2. For comparison, the total emissions by each class 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.

Table 1. Median ambient concentrations of the 24 most prevalent VOC between 6 and 9 am at urban sites from the 2002 and 2003 campaigns. For comparison, the median VOC concentrations from 39 U.S. cities and the ratios between the median MCMA/US concentrations are also shown

	Compound	**Mexico (ppbV)**	**US urban (ppbV)**	**Ratio (Mex/US)**
1	Propane	343.9	23.5	14.6
2	n-butane	164.1	40.3	4.1
3	i-pentane	69.3	45.3	1.5
4	Toluene	64.3	33.8	1.9
5	i-butane	62.7	14.8	4.2
6	C2's (ethane, ethylene, acetylene)	55.0	57.6	1.0
7	M,p-xylene	27.5	18.1	1.5
8	n-pentane	23.7	22.0	1.1
9	2-methylpentane	22.1	14.9	1.5
10	i-octane	19.0	6.8	2.8
11	1,2,4-trimethylbenzene	14.5	10.6	1.4
12	Hexane	13.7	11.0	1.2
13	3-methylpentane	13.7	10.7	1.3
14	Propylene	13.0	7.7	1.7
15	MTBE	12.3	--	--
16	Benzene	12.3	12.6	1.0
17	2,3-dimethylbutane	12.2	3.8	3.2
18	o-xylene	11.2	7.2	1.6
19	i-butene	10.1	5.9	1.7
20	3-methylhexane	9.4	5.9	1.6
21	Ethylbenzene	8.6	5.9	1.5
22	2,3,4-trimethylpentene	8.1	2.5	3.2
23	Methylcyclopentene	7.9	6.4	1.2
24	p-propylbenzene	7.2	--	--
Identified		1022.9	--	--
Unidentified		170.6	--	--
Total		**1199.8**	**439.5**	**2.7**
% identified		85.3 %	--	--

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 VOC 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 might need to be adjusted upward by factors of 2 to 3 or more, but that not all classes are necessarily overestimated. This is a relatively simplistic comparison 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.

Table 2. Comparison of measured VOC concentrations and the corresponding emission inventory VOC class for Mexico City

Model Species	**VOC median 6-9 am (ppbV)**	**% of total**	**Invent. 10^3 ton/yr**	**% of invent.**	**Adjust. factor**
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
Total	1044.5	100.0	326.5	100.0	

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 ethylbenzene/toluene ratio decreases compared to the ratio from fresh emission

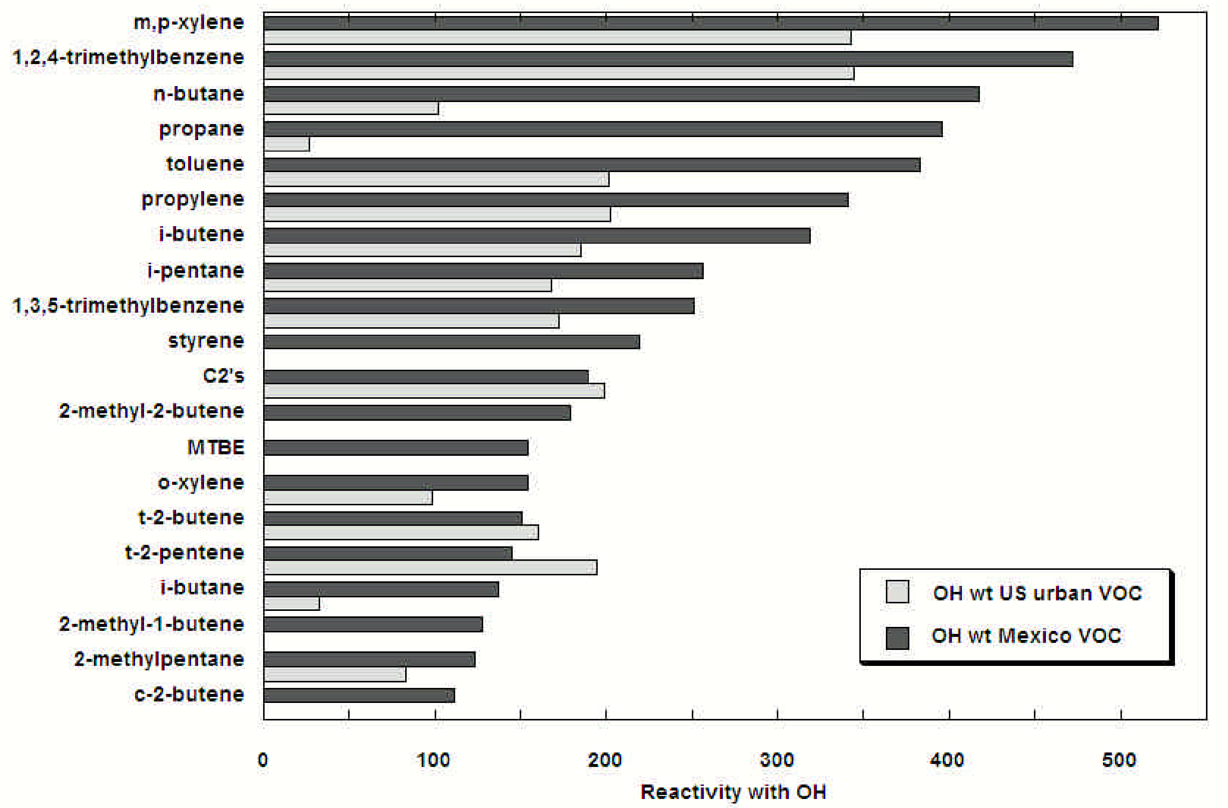

Figure 1. Distribution of VOC reactivity with OH in Mexico City and the median levels for 39 US cities.

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.

In addition to canister sampling, VOC measurements were also obtained in both campaigns using PTR-MS instruments on the mobile laboratory and at the urban tower. Figure 3 shows a comparison between GC-FID and PTR-MS responses for toluene. In general, a good agreement was found for species such as benzene, toluene, C2-benzenes and C3-benzenes. The PTR-MS has a significant advantage in detection of oxygenated VOC compared to canister methods. The combination of methods suggests that oxygenated VOC contribute an additional 20% not identified by canister sampling to the overall VOC burden of Mexico City.

Results for a number of aromatic and oxygenated VOC detected with the PTR-MS operated at the CENICA supersite are shown in Table 3. In this case, comparisons with PTR-MS measurements in Houston, Texas illustrate how much the MCMA levels are elevated compared to a polluted US city.

The FOS provides another method to obtain continuous VOC concentration measurements. As shown in Figure 4, the diurnal average profile of olefinic VOC detected with the FOS exhibits a similar profile to what would be expected for typical pollutants emitted by mobile sources, such as NO and CO (INE, 2000). The highest olefin concentrations were measured at 7:00 am and ranged from 30 to 87 ppbV, with 58 ppbV as average. This morning peak is attributed to rush hour emissions in combination with a shallow morning mixed layer. The lowest concentrations were observed during the afternoon, with an average of 6.6 ppb. The diurnal pattern was relatively constant during the entire study. There was a small difference of 6 ppbV observed between holy week (national holyday period, characterized by reduction in traffic) and the other two weeks at the morning rush hour.

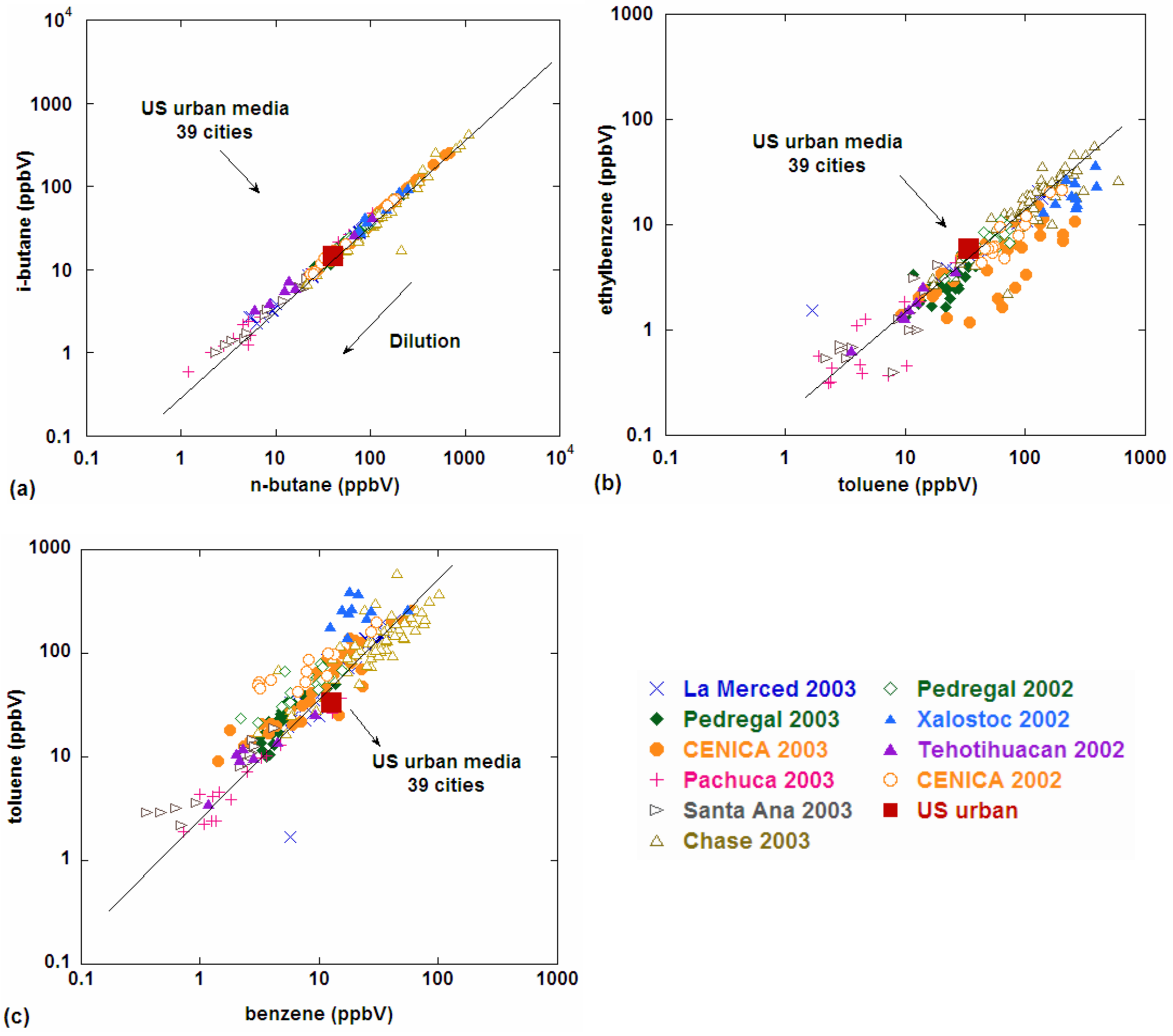

Figure 2. Ratios of specific compounds showing the effects of ambient dilution, chemistry and direct emission sources during MCMA 2002 and 2003: (a) I-butane versus n-butane, (b) ethylbenzene versus toluene and toluene versus benzene. As comparison the median value for 39 US cities is included (Parrish *et al*., 1998).

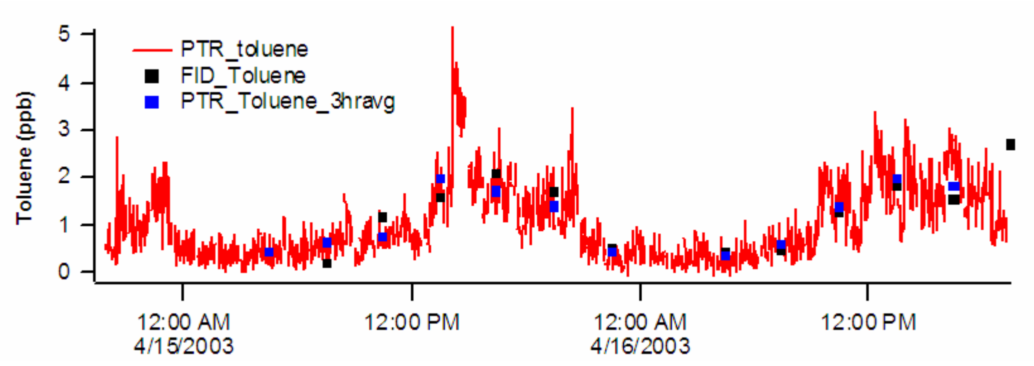

Figure 3. Comparison between GC-FID and PTR-MS responses for toluene for two days during MCMA 2003.

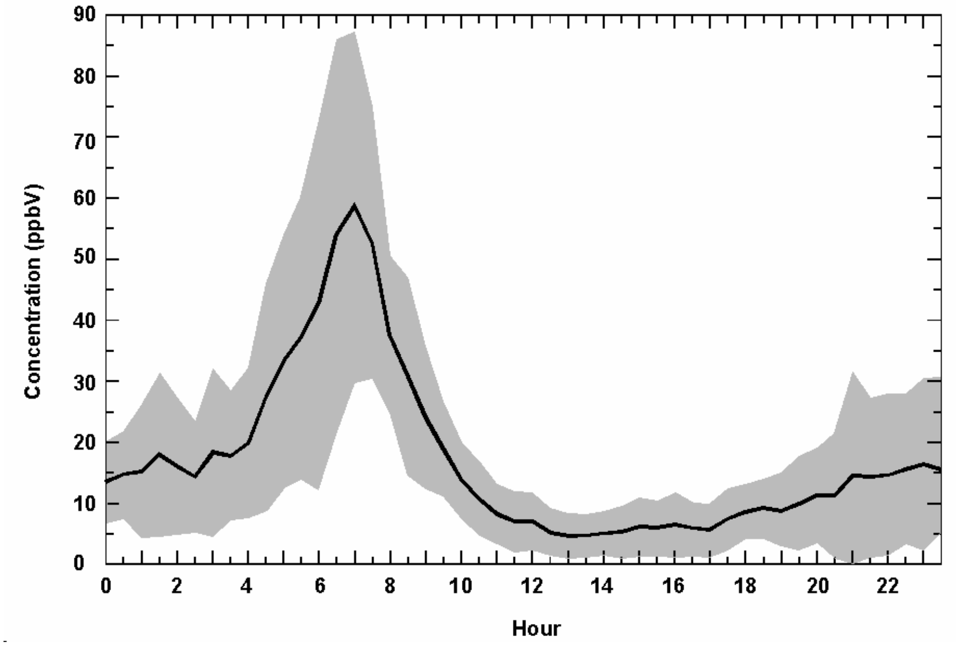

Figure 4. Diurnal average olefin concentration (as propylene) measured with the FOS from the urban tower during April, 2003. The shadow area represents ±1 standard deviation from the total average.

Table 3. Comparison of aromatic and oxygenated VOC median concentrations measured with the PTR-MS at the CENICA supersite during MCMA 2003 and in Houston, Texas

Species	Mexico (ppbV)	Houston (ppbV)	Ratio (Mex/US)
Benzene	1.65	0.34	4.8
Toluene	7.19	0.41	18
Styrene	0.21	0.01	21
C2-benzenes	3.26	0.28	12
C3-benzenes	1.67	0.37	4.5
C4-benzenes	0.38	0.20	1.9
Naphthalene	0.15	--	--
1-methylnaphthalene	0.08	--	--
Phenol	0.14	--	--
Cresols	0.08	--	--
Dimethylphenols	0.05	--	--
Methanol	23.2	6.18	7.3
Acetaldehyde	6.47	1.94	3.3
Acetone	8.01	3.25	2.5
Acetonitrile	0.73	--	--

As described before, the difficulty in using the FOS as an olefin sensor is relating response to concentration. Guenther and Hills (1998) presented FIS response factors for a number of compounds. To analyze the FOS response in the atmosphere of Mexico City we evaluated the sensitivity of 5 olefins (propylene, ethylene, isoprene, 1-butene and 1-3 butadiene) and nitric oxide. All of the olefins exhibited a response. Nitric oxide gave no response in this test. Once response factors were determined, the FOS signal was compared to the sum of olefins as measured simultaneously with the canister sampling system. Data shown in Figure 5 suggest that generally the total olefin level detected by the FOS is larger than the sum of identified olefins from canister samples. In only 3 of the 21 sample periods compared was the FOS response less than the sum of olefins measured in canister samples. With these periods removed, the ratio between the sum of olefins measured by canisters and the FOS signal shows a median of 48% which indicates that 52% of olefins detected by the FOS remain unknown. Additional analysis is needed to identify these unknown species.

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; Arriaga *et al.*, 1997). The levels of most other VOC 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

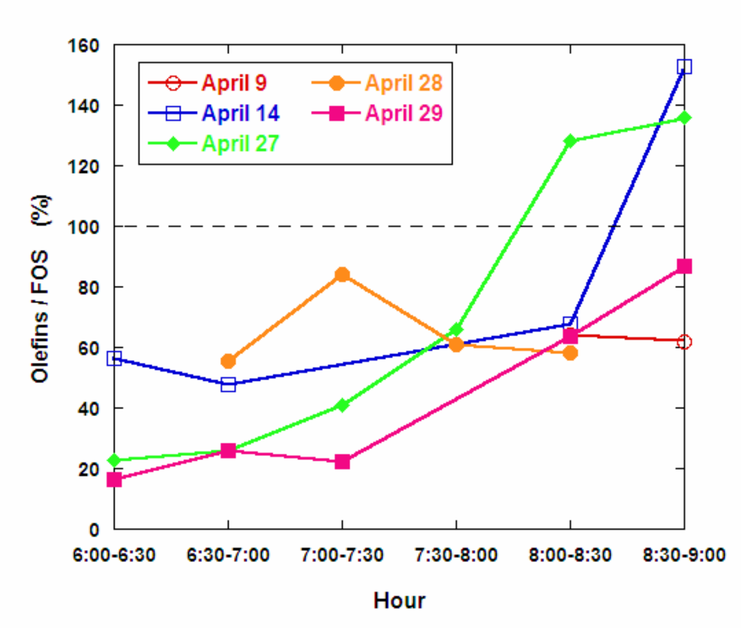

Figure. 5. Comparison of identified olefins weighted by their corresponding FOS sensitivities from GC/FID measurements versus FOS measurements for 21 sample periods during the morning rush hours.

the inventory by factors of 2 to 3. The use of ratios of individual VOC is useful for examining the effects of chemistry or nearby sources on measured VOC 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. Although additional research is required to determine what exactly the FOS response represents, the use of the FOS as olefin detector provides another way to obtain continuous VOC data.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support and assistance of Mario and Luisa Molina as the directors of the MCMA field campaigns.

REFERENCES

Arriaga, J., Escalona, S., Cervantes, A.D., Orduñez, R. and Lopez, T., 1997: Seguimiento de COV en aire urbano de la ZMCM, 1992-1996. Garcia-Colin, S. and Varela, J.R. (Eds.). In Contaminación Atmosferica II. El Colegio Nacional / Universidad Autonoma Metropolitana, Mexico, D.F.

Guenther, A. and Hills, A., 1998. Eddy covariance measurement of isoprene fluxes. J. Geophys. Res. 103, 13145-13152.

INE, JICA and CENICA, 2000. Almanaque de datos y tendencias de la calidad del aire en ciudades mexicanas. Instituto Nacional de Ecología, SEMARNAT. México D.F.

Lindinger, W., Hansel, A. and Jordan, A., 1998: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research, Int. J. of Mass Spec. and Ion Processes, 173, 191-241.

Mugica, V., Ruiz, M.E., Watson, J., and Chow, J., 2003: Volatile aromatic compounds in Mexico City atmosphere: levels and source apportionment. Atmosfera 16, 15-27.

Parrish, D.D., Trainer, M., Young, V., Goldan, P.D., Kuster, W.C., Jobson, B.T., Fehsenfeld, F.C., Lonneman, W.A., Zika, R.D., Farner, C.T., Riemer, D.D. and Rodger, M.O., 1998: Internal consistency test for evaluation of measurements of anthropogenic hydrocarbons in the troposphere. J. Geophys. Res. 103, 22339-22359.