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# Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID in Mexico City during the MCMA 2003 field experiment

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## Abstract

A comparison of aromatic hydrocarbon measurements is reported for the CENICA supersite in the district of Iztapalapa during the Mexico City Metropolitan Area field experiment in April 2003 (MCMA 2003). Data from three different measurement methods were compared, a proton transfer reaction mass spectrometer (PTR-MS), long path measurements using a UV differential optical absorption spectrometer (DOAS), and gas chromatography-flame ionization analysis (GC-FID) of canister samples. Lab tests established that the PTR-MS and DOAS calibrations were consistent for a suite of aromatic compounds including benzene, toluene, p-xylene, ethylbenzene, 1,2,4-trimethylbenzene, phenol, and styrene. The point sampling measurements by the PTR-MS and GC-FID showed good correlations ($r$=0.6), and were in reasonable agreement for toluene, $C_2$-alkylbenzenes, and $C_3$-alkylbenzenes. The PTR-MS benzene data were consistently high, indicating potential interference from fragmenting alkyl aromatics for the 145 Td drift field intensity used in the experiment. Correlations between the open-path data measured at 16-m height over a 860 m path length (retroreflector in 430 m distance), and the point measurements collected at 37-m sampling height were best for benzene ($r$=0.61), and reasonably good for toluene, $C_2$-alkylbenzenes, naphthalene, styrene, cresols and phenol ($r>0.5$). While the DOAS data agreed within 20% with both point measurements for benzene, concentrations measured by DOAS were on average a factor of 1.7 times greater than the PTRMS data for toluene, $C_2$-alkylbenzenes, naphthalene, and styrene. The level of agreement for the toluene data was a function of wind direction, establishing that spatial gradients – horizontal, vertical, or both – in VOC mixing ratios were significant, and up to a factor of 2 despite the fact that all measurements were conducted above roof level. Our analysis highlights a potential problem in defining a VOC sampling strategy that is meaningful for comparison with photochemical transport models: meaningful measurements require a spatial fetch that is comparable to the grid cell size of models, which is typically few 10 km$^2$. Long-path DOAS measurements inherently average over a larger spatial scale than

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point measurements. The spatial representativeness can be further increased if observations are conducted outside the surface roughness sublayer, which might require measurements at altitudes as high as few 10 m above roof level.

## 1 Introduction

The Mexico City Metropolitan Area (MCMA-2003) field experiment conducted in the spring of 2003 was an extensive and collaborative scientific effort to update and improve the local emissions inventory, and to gain a better understating of the chemistry and transport processes driving atmospheric pollution in Mexico City (Molina et al., 2007). Mexico City is one of the world's largest cities and has frequent and severe air quality problems owing to the large number inhabitants (∼19 mio.), industrial growth (more than 53 000 industries) and transport needs (∼3.5 mio. vehicles), in addition to its own topography and meteorology. Mexico City lies in an elevated basin (2240 m above sea level) surrounded by mountain ridges. Its high elevation and relatively low latitude (19°25′ N) lead to intense sunlight promoting photochemical processes that drive the formation of ozone, airborne particulate matter (PM) and other oxidants.

One of the central precursors to both ozone and PM formation are volatile organic compounds (VOCs). The emissions of these compounds are enhanced in Mexico City by the less efficient combustion processes due to the high altitude, as well as the subtropical weather with intense solar radiation that accentuate the evaporative emissions from a variety of sources such as storage and distribution of gasoline, solvent-base cleaning, painting, and industrial processes. Sparse vegetation in Mexico City means biogenic VOCs emissions are small in comparison to the anthropogenic VOC emissions (Velasco, 2003). During daytime the intense and continuous anthropogenic emissions of NO and VOCs in combination with the high OH reactivity generate ozone at rates exceeding 50 ppbv $h^{-1}$ as early as one hour after sunrise (Shirley et al., 2006). The rapid formation of glyoxal observed after sunrise by Volkamer et al. (2005) during the MCMA-2003 experiment indicate an efficient VOC oxidation process during morning hours, and the high glyoxal level observed until early afternoon reveals a persistently active VOC chemistry during most of the day. Hydrocarbon oxidation products resulting from these VOC oxidation processes contribute significantly to the formation of secondary organic aerosols, much faster and an order of magnitude larger than expected previously (Volkamer et al., 2006, 2007; Kleinman et al., 2007; Dzepina et al., 2009).

The vast suite of compounds that are present in urban air and their photochemical products makes assessing specific VOC burdens a difficult analytical task. Since no single technique can provide speciated measurements of all the VOCs needed for modeling their impact on urban air photochemistry, different measurement techniques are often used in combination to provide measurements of as many types of species as possible. During the MCMA-2003 VOC measurements were made at different locations inside and outside of Mexico City, including a supersite at the roof top of the Mexican National Center for Environmental Research and Training (CENICA) in the district of Iztapalapa. Four distinct analytical techniques were used to measure VOCs at this site: whole air canister samples with gas chromatography/flame ionization detection (GC-FID), on-line chemical ionization using a Proton Transfer Reaction Mass Spectrometer (PTR-MS), continuous real-time detection of olefins using a fast isoprene sensor (FOS) calibrated with a propylene standard, and long path measurements using UV differential optical absorption spectroscopy (DOAS). The simultaneous use of these techniques provided a wide range of individual VOC measurements with different spatial and temporal scales. Such a situation presents a clear need for a comparison of the measurement techniques to verify the data can be combined into a single comprehensive data set.

Formal international comparisons between research groups using gas chromatography based systems for the measurement of non-methane hydrocarbons have been reported (Apel et al., 1994, 1999, 2003; Slemer et al., 2002; Volz-Thomas et al., 2002). These studies demonstrated that different calibration standards and analytical procedures could lead to significant differences between laboratories in the analysis of synthetic mixtures and ambient air samples. Analysis problems such as the co-elution of components, losses of volatile $C_2$ components, and adsorptive losses of $C_7$–$C_9$ components contributed to measurement uncertainty. The best level of agreement was achieved between the most experienced laboratories and was within ±20% for most compounds in synthetic mixtures and ambient samples (Volz-Thomas et al., 2002). The analysis of oxygenated species is even more problematic (Apel et al., 1998; Fujita et al., 2003) and there have been fewer systematic investigations on the comparison of techniques and data for these species. Kuster et al. (2004) reported on the results of an informal comparison of ambient data from in-situ gas chromatography based systems and a PTR-MS instrument that include both non-methane hydrocarbons and oxygenated species.

There are relatively few reports comparing DOAS based measurements with other VOC measurement techniques. Barrefors (1996) reported a very poor correlation between a commercial DOAS instrument measurement of benzene and GC based measurements for an urban environment ($r=0.18$). Toluene measurements displayed a much better correlation ($r=0.71$) but the DOAS measurements were ~ factor of 2 higher. Kim (2004) reported a comparison between a commercial DOAS system and commercial in-situ GC-FID system for the measurement of benzene, toluene, and the sum of the xylene isomers in a suburban area. In that study benzene data compared very poorly ($r=0.128$) and were essentially uncorrelated because mixing ratios were at the detection limit of the DOAS instrument. Regressions between the DOAS and GC data for toluene and xylenes showed significant scatter but were reasonably well correlated, with toluene displaying the best overall correlation and level of agreement.

More recently Velasco et al. (2007) have reported intercomparison results between PTR-MS, GC-FID a commercial DOAS and a research-grade DOAS from auxiliary monitoring sites in Mexico City during the MCMA-2003 field experiment. At these sites PTR-MS and canister/GC-FID measurements were made during three or four days. One of these sites included benzene and toluene measurements with a commercial DOAS. In spite of the fact that GC-FID and PTR-MS consisted of point measurements while the DOAS measured over a long path, the comparison showed good agreement, with the exception of benzene measurements by the commercial DOAS, which differed from PTR-MS and GC-FID measurements in the early afternoon, when ozone levels are high. The presence of ozone is not a problem for the DOAS technique, as was demonstrated in that work from the research grade DOAS data, which did not show the high benzene offset during afternoons, and showed excellent correlation between benzene, toluene, m-xylene and p-xylene. This paper presents results from a more detailed comparison of PTR-MS, GC-FID, and research-grade DOAS measurements of VOCs at the CENICA supersite during MCMA-2003. These techniques measured several aromatic species in common over a period of 4 weeks, and provide a much larger data set for a statistically robust analysis.

## 2 Experimental

### 2.1 Sampling location and description

Measurements were made at the CENICA supersite in Iztapalapa, a suburb of Mexico City with a high population density (more than 12 000 inhabitants per km$^2$) in a mixed area with residences, light and medium industries, services and commerce. Instruments were housed in an air conditioned shelter on the roof of the CENICA building. The PTR-MS and canisters sampled air from a 25-m walk-up scaffold tower erected on the roof-top. Air from the top of the tower was pulled down through a 5/8′′ diameter Teflon sampling line at 45 SLPM into the shelter where it was sub-sampled by a number of instruments including the PTR-MS and canister filling system. These measurements thus represent point samples from a 37-m height. The DOAS technique in contrast measures VOC integrated over an 430 m air column. The DOAS instrument was also housed in the same shelter and directed its beam at a retro reflector mounted 16-m above the ground on a radio tower 430 m to the south-south-east. Measurements were made at CENICA from 3 April to 2 May 2003 although the instruments were operating at different times with different sampling frequencies. Table 1 shows the species that were measured in common. Specifics on the individual instruments and measurement methods are described below.

## 2.2 PTR-MS

A PTR-MS instrument (Ionicon Analytik) was used to monitor a number of species. This technique has been described in detail previously (Hansel et al., 1995; deGouw and Warneke, 2007). The technique identifies VOCs by molecular weight and is insensitive to the major components of air and also to several light hydrocarbons ($C_2$–$C_6$ alkanes, ethene, acetylene). Given current knowledge of atmospheric VOC composition, primarily accumulated over the last 20 years using chromatography based techniques, there are a number of VOCs that are suited to monitoring by PTR-MS because of the uniqueness of their molecular weight and predominance in the atmosphere. A basic issue with the technique is that a number of species dissociate upon protonation and mass fragments can cause interferences at other masses. Also, the technique can not resolve geometric isomers and is subject to isobaric interferences. For example, the xylene isomers ($C_8H_{10}$) can not be distinguished from ethylbenzene ($C_8H_{10}$) and instead the sum of the substituted alkyl benzene species with molecular weight of 106 amu ($C_2$-alkylbenzenes) are reported. Benzaldehyde ($C_7H_6O$) is also detected at the same mass and is considered an isobaric interference for the $C_2$-alkylbenzenes determination. These issues require that the PTR-MS technique be verified against GC based measurements in different environments until there is a better understanding of the veracity of the PTR-MS measurement approach for complex organic mixtures such as urban air. The advantages of the PTR-MS are the sampling frequency, the limited sample handling – hence the ability to measure oxygenated species otherwise difficult to determine with canister based sampling approaches – and the relative ease and cost effectiveness of data work-up. During MCMA-2003 the PTR-MS was operated using a 2.1 mbar ion drift pressure and a drift field intensity of 145 Td. Twenty-two organic ions were monitored during the study. Table 1 shows a partial list of the ions monitored and the species represented by these ions for those species measured in common by the DOAS and GC-FID techniques. Laboratory measurements of the vapour from pure compounds confirm that phenol and cresols did not fragment in the PTR-MS and thus could be quantified using their M+1 ion abundance.

The PTR-MS sensitivity was determined with a multicomponent compressed gas standard from Apel-Reimer Environmental (Denver, USA) containing hydrocarbons (benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, acetonitrile, isoprene, and a-pinene), and oxygenated species (methanol, acetaldehyde, acetone, 2-butanone, methacrolein, methylvinylketone). The standard had a stated accuracy of ±2% for hydrocarbons and ±5% for oxygenated species. The gas standard was dynamically diluted with humid zero air that was continuously produced by a custom zero air generator consisting of a heated tube (300°C) packed with platinum pellets (1% weight on alumina spheres). Multipoint calibrations were performed every couple of days. The p-xylene and 1,2,4-trimethylbenzene sensitivities were used to represent the average group sensitivity for the sum of $C_2$-alkylbenzenes and $C_3$-alkylbenzenes, respectively.

The phenol sensitivity was determined in the laboratory using a permeation tube, 567 ng/min±2% (VICI Metronics) and referenced against toluene sensitivity determined from the compressed gas standard. Flows from the permeation device and the compressed gas standard were mixed and then dynamically diluted with humid zero air (~46% RH at 22°C). The measured phenol-to-toluene sensitivity ratio was determined to be 1.3 and this ratio was used for field calibrations. This measured sensitivity ratio was comparable to the calculated sensitivity ratio of 1.2 determined from the ratio of their collisional rate coefficients with $H_3O^+$ (Su and Chesnavich, 1982; Su, 1989) Given their small difference in mass and hence small difference in ion transmission efficiency, difference in sensitivity between toluene and phenol were attributed to differences in reaction kinetics. We observed that phenol displayed a humidity dependent sensitivity under these drift conditions. Dry zero air calibrations performed in the lab yielded sensitivities ~25% lower than the humid air calibrations.

Cresol sensitivity was referenced to the sensitivity of p-xylene. The calculated collisional rate coefficients for the cresol isomers average 10% larger than that of p-xylene. Styrene sensitivities were assumed to be equal to those of p-xylene since their calculated collisional rate coefficients and ion masses were similar. Likewise, naphthalene sensitivity was assumed to be equivalent to that of 1,2,4-trimethylbenzene since the rate coefficients and ion masses were similar.

Partial fragmentation of mono-alkyl aromatics such as ethylbenzene occurs under the ion drift conditions used here. Mass scans of ethylbenzene show a dominant M+1 ion but also a significant ion at *m/z*=79 (40%). This fragmentation produces a positive artifact for PTR-MS benzene measurements and causes the PTR-MS to underestimate $C_2$-benzenes. The magnitude of this effect can be calculated from known abundances of $C_2$-alkylbenzenes isomers reported in the literature and also measured at CENICA by GC-FID. The GC-FID measurements at CENICA and those reported elsewhere in urban environments (i.e. Jobson et al., 2004) indicate that ethylbenzene comprises about 20% of the $C_2$-alkylbenzenes abundance. Given the fragmentation of ethylbenzene and its relative abundance, the PTR-MS measurements underestimated $C_2$-alkylbenzenes abundance by ∼8%. Similarly, given that the molar abundance of $C_2$-alkylbenzenes are typically greater than those of benzene by approximately a factor of 2 in urban air, the PTR-MS measurements of benzene were over estimated by ∼16%.

The PTR-MS was operated in two different measurement modes reflecting differences in the number of ions measured and the dwell times used. In the middle third of the experiment the instrument was used in a VOC flux study (Velasco et al., 2004). During this period (10–16 April) only four analyte ions were monitored (33, 59, 93, 107) at a high time resolution (0.2 s dwell time). For the remainder of the study (4–9 April, 22 April–1 May) single ion monitoring was done on about 12 masses with dwell times ranging from 2 to 5 s, resulting in about 1 min sample intervals. A turbopump failure occurred midway through the study and there is no data from 17 to 21 April.

Backgrounds for the PTR-MS were performed automatically by sampling air from the zero air generator. Ambient data were well above detection limits for most species. In the ambient mode of operation detection limits were estimated to be ∼100 pptv for benzene, toluene, $C_2$-alkylbenzenes, and $C_3$-alkylbenzenes. Detection limits for phenol, cresols, styrene, and naphthalene were estimated from the signal to noise ratio of the raw data during stable clean air periods. For phenol, cresols, and styrene the detection limit was approximately 50 pptv, while for naphthalene it was approximately 60 pptv. At these mixing ratios the 1 sigma variation about the mean was 50%. The ambient data for these species was occasionally near the detection limit, especially for cresols.

### 2.3 DOAS

Two long path differential optical absorption spectroscopy (LP-DOAS) instruments were installed on the rooftop of the CENICA building. The DOAS technique has been described elsewhere (Platt, 1994). In brief, light from a broadband UV/vis lightsource (Xe-short arc lamp) is projected into the open atmosphere onto a distant array of retro reflectors, which folds the lightpath back into the instrument where spectra are recorded using a Czerny-Turner type spectrometer coupled to a 1024-element PDA detector. Only data from DOAS#1 will be presented here, DOAS#2 is described elsewhere (Volkamer et al., 2005). Both instruments were operated by the CU Boulder/MIT team. The light path of DOAS#1 was directed towards a telephone antenna tower in a south-easterly direction at an average height of 16 m with a 430 m path length (total 860 m). DOAS#1 measured $O_3$, $NO_2$, $SO_2$, HONO, HCHO, benzene, toluene, m-xylene, p-xylene, mono-substituted alkylbenzenes ($C_2$ and higher), phenol, p-cresol, and benzaldehyde by observing the unique specific narrow-band (<5 nm) absorption structures of these molecules. Also naphthalene and styrene were measured for the first time with DOAS in the atmosphere (Flores et al., 2004). Spectra were recorded by sequentially observing 40-nm wide wavelength intervals in the wavelength range between 240 nm and 375 nm at 0.2 nm FWHM spectral resolution. The time resolution of recording a full cycle of spectra varied between 30 s and 4 min, depending on the abundance of UV-light absorbing ozone. Reference spectra of aromatic compounds were recorded by introducing quartz-cuvettes filled with vapor into the light beam, and these spectra were calibrated to absorption cross-section spectra taken from the literature (Etzkorn et al., 1999). Absorptions of atmospheric oxygen were eliminated using the interpolation approach of Volkamer et al. (1998). In brief, saturation of molecular absorption lines of oxygen in the Herzberg I–III bands were modeled in high-resolution using line parameters from (Fally et al., 2000; Jenouvrier et al., 1999; Merienne et al., 2000, 2001) and oxygen column densities of $3.7\times10^{17}$ molecules cm$^{-2}$ and $4.1\times10^{17}$ molecules cm$^{-2}$ to bracket the effect of density variations on oxygen column densities. The collision induced absorption of oxygen in the Wulf bands was fitted using the literature spectra from (Bernath et al., 1998). For ozone, temperature dependent absorption cross-sections (Bass and Paur, 1981) for 293 K and 313 K were convoluted to match the spectral resolution of the instruments, and fitted simultaneously with other trace-gas reference spectra and a fifth order polynomial high-pass filter to account for broadband molecule and aerosol extinction using non-linear least squares fitting routines (Stutz et al., 1996; Fayt et al., 2001). The mean detection limits were: 1.3 ppbv ($O_3$), 1.5 ppbv ($NO_2$), 0.26 ppbv ($SO_2$), 0.5 ppbv (HONO), 5 ppbv (HCHO), 1 ppbv (benzene, toluene, m-xylene), 0.3 ppbv (p-xylene), 1.8 ppbv (ethylbenzene-equivalents), 0.5 ppbv (styrene), 0.06 ppbv (phenol, p-cresol), 0.2 ppbv (benzaldehyde), 0.08 ppbv (naphthalene).

While DOAS measurements allow for the selective detection of xylene-isomers, only m- and p-xylene were sufficiently abundant to be detected. Since the other techniques compared here are not isomer-specific, xylene isomers and ethylbenzene were summed to calculate total $C_2$-alkylbenzenes, accounting for the fact that other n-alkyl benzenes and ethylbenzene have similar UV absorption features (Axelsson et al., 1995). A formula was derived to estimate the sum of the $C_2$ benzenes based on the abundance of the measured isomers and the apparent correction required for DOAS measurements of ethylbenzene to bring them into agreement with the GC-FID analysis of canisters collected at CENICA.

$$\sum C_2\text{-alkylbenzenes} = 1.4 * (\text{m-xylene} + \text{p-xylene}) + 0.21 * \text{ethylbenzene} \qquad (1)$$

### 2.4 Canister analysis by GC-FID

44 samples were collected in electro-polished stainless-steel canisters. The canisters were filled over a 30 min period with an automated sampler (Xon Tech, Inc. model 910PC). Approximately 60% of the samples were collected between 06:00 and 09:00 LT when VOC concentrations were highest due to roadway traffic emissions. The remaining samples were collected during the rest of the morning and early afternoon. All samples were analyzed on site within 24 h of sampling using an Agilent 6890 gas chromatograph with flame ionization detection. Air samples were cryogenically preconcentrated on a glass bead packed trap and analyzed on a 30-m DB-1 column (0.32 mm i.d. and 1 µm phase thickness). The detector response was calibrated with a NIST traceable standard of 2,2-dimethylbutane (stated accuracy ±10%). The detection limit was calculated to be 20 pptC.

## 3 Results and discussion

### 3.1 PTR-MS versus GC-FID

There were a total of 43 canisters that were collected when the PTR-MS was operating. Canisters were filled on 9, 13, 14, 27, 28, and 29 April. Only toluene and $C_2$-alkylbenzenes data from the PTR-MS were available for 13 and 14 April. The PTR-MS data were averaged over the 1/2 h canister fill times. Figure 1 shows the toluene time series for four of these days to illustrate the temporal variability and level of agreement between the two measurements. Occasionally there were large changes in concentration over the canister fill period, reflected by a large standard deviation in the PTR-MS averaged data.

A number of canister data from 28 and 29 April had low values for several species. This is clearly evident in the toluene data of Fig. 1 for the 4 samples collected on 29 April. Even larger deviations were noted for $C_2$-alkylbenzenes and $C_3$-alkylbenzenes.

To evaluate this discrepancy a comparison of data sets was performed by comparing hydrocarbon to benzene correlations. This is illustrated in Fig. 2 for the $C_2$-alkylbenzene data. One would anticipate a strong correlation between aromatic hydrocarbons and benzene mixing ratios in urban areas since these species have similar sources. An analysis of hydrocarbon ratios can be an effective means of screening data for quality (Parrish et al., 1998). As shown in Fig. 2, the averaged PTR-MS data defined a compact linear relationship with a slope of 1.98±0.7 and Pearson correlation coefficient $r=0.978$. The GC-FID data also defined a liner trend though several samples collected on 28 and 29 April, but displayed much lower $C_2$-alkylbenzene-to-benzene ratios that the rest of the data. These same canister samples also yielded anonymously low $C_3$-benzene to benzene ratios. It appears that heavier hydrocarbons ($C_7$–$C_9$) were lost in the collection or analysis for these samples. The cause of this was not clear. These data were labeled as "outliers" and excluded from the comparison.

Plots of averaged PTR-MS data versus canister/GC-FID data are shown in Fig. 3. The data were fit with a monovariate linear regression weighted by the standard deviation of the PTR-MS data. The results of these fits are shown in Table 2. Most of the data fell within 20% of the 1:1 line and the slopes of the regression fits were close to unity. Regression through the benzene data yielded a significant positive intercept, suggesting the possibility of positive interferences for PTR-MS benzene data. As noted earlier, this mass experiences positive interference from fragmenting alkyl aromatics, notably ethylbenzene. Fragmenting ethylbenzene would cause PTR-MS benzene data to be overestimated by ∼16%, an error that would be reflected in the slope. Other alkyl substituted benzenes, such as *n*-propylbenzene may also fragment, so the 16% overestimation is a lower limit. The intercept, however, indicates the presence of a systematic bias in one of the techniques. The PTR-MS to GC-FID benzene ratio was 1.1 at the highest benzene ratios (>6 ppbv), but displayed more variability and a tendency to increase at lower mixing ratios (<4 ppbv). For the lower mixing ratios, the average PTR-MS to GC-FID ratio was 1.8±0.6. The reason for this large and variable difference could not be identified. The results for styrene are not shown as there was a poor correlation between the data sets, likely due to a co-elution problem on the DB-1 column.

## 3.2 DOAS versus GC-FID

The comparison between the DOAS data averaged over the 1/2 h canister collection times and the GC-FID analysis of the canisters are displayed in Fig. 4. The level of agreement for benzene was reasonable with most data scattered about the 1:1 line. A linear regression through the data, excluding data below the 1 ppbv DOAS detection limit, weighted by the standard deviation of the DOAS data, yielded a slope of 0.84±0.05 and an intercept of 0.84±0.09, though it is noted that this intercept is compatible with zero within the DOAS detection sensitivity. The average DOAS to GC-FID benzene ratio was 1.4±0.5. The DOAS toluene and $C_2$-alkylbenzene data were frequently much higher than GC-FID measurements and overall displayed a greater variability than the PTR-MS versus GC-FID plots. This may indicate a general problem in comparing point sampling to long path sampling for reactive hydrocarbons because of significant spatial gradients in urban areas. This point will be explored below. The regression fits to the data are given in Table 2. The average DOAS to GC-FID ratio for toluene was 2.0±1.6. For $C_2$-alkylebenzes the average ratio was 2.4±1.4. We note that there was a poor level of agreement for the styrene data with most of the DOAS data below detection limits for these sampling periods.

## 3.3 PTR-MS versus DOAS

### 3.3.1 Lab tests of synthetic mixtures

The potential level of agreement between the PTR-MS and DOAS measurements for aromatics was assessed based on analysis of trace gas concentrations in both single and multicomponent mixtures prepared in the lab. In these experiments, a glass bulb was evacuated and filled to a known pressure with the vapor from a vial containing the pure compound (>98%). The bulb was back filled with He to a 1000 torr pressure. A 10 cm cuevette was filled from the bulb and the UV/Vis absorbance spectrum recorded on a Shimadzu UV-2501PC Ultraviolet-Visible spectrometer. The bulb concentration was calculated using the DOAS technique from the recorded spectrum. Immediately after recording the UV/Vis spectrum the bulb mixture was diluted with dry air in a dynamic flow system and the output measured by the PTR-MS. Dilution by a factor of 10 000 or more was necessary to bring the high concentration bulb mixture to within the analytical range of the PTR-MS instrument. Flow rates through the mass flow meters were calibrated against a primary standard with an accuracy of 0.25% (DryCal ML-500, BIOS International Corp). The experimental set-up is shown in Fig. 5. A least three levels of dilution were performed for each compound spanning about a factor of 10 range in mixing ratios. The PTR-MS was calibrated with the same multi-component VOC standard and procedure used in the field calibrations. For these tests the standard was diluted in dry zero to match the matrix of the bulb diluent. The phenol sensitivity was determined with a permeation device diluted with dry zero air. A plot of measured mixing ratios by PTR-MS versus calculated DOAS mixing ratios was made for each compound as shown in Fig. 6. The DOAS values were calculated from the measured concentrations in the bulb multiplied by the respective dilution factor. Naphthalene and phenol required a long time before transfer lines became equilibrated and a stable PTR-MS signal was observed. With the exception of naphthalene, the PTR-MS measurements agreed with the UV/Vis calculated concentrations for dry conditions within the experimental uncertainty of the respective determinations. The regression results are shown in Table 3. It was concluded that the calibrations of the two systems were consistent. Naphthalene was difficult to work with due to its low vapour pressure. The PTR-MS observed higher naphthalene concentrations than the DOAS calculations. This may have been due to loss of naphthalene to the UV/Vis cuevette during sample transfer.

### 3.3.2 PTR-MS versus DOAS regressions

The DOAS and PTR-MS measured VOCs on different temporal and spatial scales. While time averaging allows data collected at different frequencies to be compared, it is not at all clear how well a point measurement will agree with a long path measurement in an urban area, in particular for reactive hydrocarbons emitted from multiple sources. At issue is the potential for concentration gradients between the average concentration along the DOAS beam and the highly localized measurements by PTR-MS. Figure 7 illustrates the level of agreement for a two day period for benzene and toluene. Overall the DOAS and PTR-MS follow each other remarkably well. Occasionally short term high concentration "plumes" appear in the PTR-MS data, likely reflecting the impact of a local (undiluted) source on the point measurement.

The PTR-MS and DOAS data were averaged over fixed 10 min intervals and the data compared in a regression analysis. Averages were calculated if there where more than 3 data points in the interval. Other averaging intervals were investigated and it was determined that time averaging did not influence the slope of the PTR-MS versus DOAS linear regression. Longer averaging intervals reduced the scatter and increased the correlation coefficient as expected. Figure 8 shows the correlation between these techniques for the 10 min averaged data. Compared to the PTR-MS versus GC-FID plots, a higher degree of scatter is evident, likely a reflection of the inherent differences in the spatial sampling between point and long path measurements. The data were fit using both monovariate and bivariate linear regressions using the standard deviation of the 10 min averages as weighting. There were some significant differences in the derived slope and intercept between the two regression methods. The results are tabulated in Table 4. It is clear that the relatively large dynamic range spanned by the data and the presence of a few points at high mixing ratios influence the monovariate linear regression fits to the point where the fits sometimes did not represent the bulk of the data. A good example is the phenol plot. The styrene and cresol data were too scattered for the bivariate regression fit to converge properly. This is probably due to the quite heterogeneous picture in the styrene time series data, which did not show the pronounced traffic pattern of high concentrations during morning rush hour, followed by dilution during the day that was typical for the other aromatics. Sources other than traffic seem to contribute to the abundance of styrene in Mexico City, and affect the DOAS and point measurements at different times, leading to poorer correlations.

An alternative approach for comparing these data sets is to examine the frequency distribution of the PTR-MS/DOAS ratio and examine the dependence of this ratio on other factors such as mixing ratio levels, time of day, and wind direction. Figure 9 shows the PTR-MS/DOAS ratio versus the DOAS measurement together with histograms of the ratio. The histograms are restricted to data where the DOAS measurements were above detection limits as defined in the experimental section. Toluene was the only species measured were the data from both instruments were clearly above detection limits during the entire study period. There was a clear tendency in the data for the PTR-MS/DOAS ratio to increase with decreasing DOAS mixing ratios, consistent with stronger mixing in the afternoon reducing spatial gradients between the two instruments. The histograms of the PTR-MS/DOAS ratio were fit with a log-normal curve and the mean ratio and standard deviation determined by the fit are given in Table 5. The mean ratio agreed well with the slope of the bivariate fit regressions for benzene, toluene, $C_2$-alkylbenzes, and naphthalene. For most species the PTR-MS/DOAS ratio was significantly less than 1. Interestingly, the mean ratio for toluene, $C_2$-alkylbenzens, and naphthalene, compounds with significant roadway emission sources, were 0.62, 0.50 and 0.57, respectively. The styrene ratio was determined to be 0.77. The cresol ratio was 0.88 and we note again that the DOAS was measuring p-cresol while the PTR-MS measures the sum of all cresol isomer and thus a ratio >1 would be anticipated. The anomalous results appear to be those for benzene and phenol which yielded mean ratios larger than 1. The phenol regression fits gave slopes less than 1, in contrast to the mean ratio found from the histogram plots. From Fig. 8 it is clear that the bulk of the PTR-MS phenol data lies above the 1:1 line and thus the mean ratio value of 1.49 is a better representation of the level of agreement. The fidelity of phenol, cresol, and naphthalene measurements by PTR-MS is not well established and this is the first reported comparison with another technique. For benzene the ratio was 1.14. This value is consistent with the product of the average PTR-MS to GC-FID benzene ratio of 1.8 multiplied by the average GC to DOAS benzene ratio of 0.71. We conclude the PTR-MS was overestimating benzene mixing ratios.

### 3.3.3 Influence of wind direction

Of the species measured in common toluene was considered to be the most accurately determined, being free from major interferences in both techniques and above detection limits during the entire study period. Lab tests also demonstrated that the PTR-MS calibration standard was in agreement with the DOAS based method. Thus ambient data should be in good agreement. However this was not the case, the PTR-MS data were often lower, suggesting a real difference between point and long path measurements due to spatial gradients in toluene mixing ratios. To better understand the general nature of the ~factor of 2 discrepancy between the DOAS and PTR-MS measurements the toluene data were sorted according to time of day and wind direction measured on the flux tower (37-m height). The toluene data were averaged over half hour intervals and the ratio of the PTR-MS to DOAS values calculated. It was clear that wind direction played some role in the level of agreement between the DOAS and PTR-MS. Figure 10 shows the frequency distribution of the DOAS/PTR-MS toluene ratio sorted according to the wind rose quadrants. The frequency distributions from the south and east sectors displayed a similar shape and mode and these data were binned together, yielding a distribution with a mean PTR-MS to DOAS ratio of 0.59±0.01. Likewise the similar frequency distributions of the north and west quadrant data were grouped, yielding a mean ratio of 0.67±0.01, significantly higher than the other data. The toluene measurements between the two techniques were in better agreement when the wind flow was from the north (315°–45°) or west (225°–315°). On the local scale major roadways lie to the east and south of the site in the general direction of the DOAS retro-reflector. VOC emissions rates were generally larger in the eastern sector traversed by the DOAS beam line (Velasco et al., 2005). The DOAS measurements likely yielded higher VOC mixing ratios that point measurements from the top of the flux tower because the DOAS beam traversed a major emissions area and was closer to the surface.

The comparison of point and long path measurements raises the interesting issue of describing average urban concentrations of primary pollutants which may have very strong local concentration gradients. Such comparisons highlight spatial heterogeneity of pollutants on the local scale. The measurements made at the top of the tower are high enough above the roughness sublayer, in which emissions are blended by the urban turbulence, that the fetch was estimated to extend in average 1.3 km. A maximum fetch of 5 km occurred at nighttime under stable conditions and minimum of 500 m under unstable conditions (Velasco et al., 2005). Thus when winds change direction, the tower measurements respond to emissions fluxes from the areas defined by the fetch. The DOAS beam inherently samples over a larger spatial scale than a point measurement if measurements are conducted at comparable height. While all measurements were conducted above roof-top level, the DOAS beam was at a lower height and pointing through a higher emission sector. We cannot rule out that vertical gradients, in addition to horizontal inhomogeneities, contribute to the systematic differences found between the open-path and point sampling techniques.

## 4 Conclusions

Measurements of aromatic compounds were made at the CENICA supersite, an urban area of Mexico City, from 3 April to 2 May 2003 by a PTR-MS instrument, a research grade DOAS instrument, and by canister sampling followed by GC-FID analysis. The PTR-MS and canisters sampled from an inlet 37-m above the ground, while the average DOAS beam height was 16-m along a 430 m path length to the south-east. The PTR-MS benzene data were typically greater than GC-FID determinations, on average by a factor of 1.8±0.6 for benzene mixing ratios <4 ppbv. At higher mixing ratios there was better agreement. The PTR-MS measurements of toluene, $C_2$-alkylbenzenes and $C_3$-alkylbenzenes were in reasonable agreement with the GC-FID data. This established the fidelity of PTR-MS data for these compounds and therefore a reasonable expectation that a comparison of PTR-MS and DOAS data for toluene and $C_2$-alkylbenzenes would also be in reasonable agreement. Reasonable agreement was observed for benzene, however, the PTR-MS and GC-FID data for toluene and $C_2$-alkylbenzenes, sampled about 20 m above the mean height of the DOAS beam, tended to be lower than the DOAS data. On average the difference was $\sim$ factor of 2 for the PTR-MS data. Lab tests established that the DOAS and PTR-MS calibrations for benzene, toluene, phenol, styrene, p-xylene, ethylbenzene, and 1,2,4-trimethlybenzene were consistent within 10%. Higher DOAS values were therefore likely caused by vertical in addition to horizontal gradients in VOC concentrations. Toluene was the best determined compound, being free of major known interferences and always above detection limits for both instruments. An analysis of the toluene data revealed that the level of agreement between the PTR-MS and DOAS was dependent on wind direction. For the entire data set the PTR-MS/DOAS toluene ratio was found to be log-normally distributed, with a mean ratio of 0.62. The toluene ratio was 0.59±0.01 when the when blew from the south and east quadrants, an area of major roadways, and 0.67±0.01 when wind blew from the cleaner north and west quadrants. This dependence on wind direction provides evidence that differences in PTR-MS and DOAS data were due to real differences in spatial gradients of VOCs. The DOAS data likely observed higher mixing ratios due to the difference in sampling height above roof-level, and the fact the light path traversed an area of major roadways. PTR-MS data for $C_2$-alkylbenzenes and naphthalene, compounds associated with roadway emissions, were on average a factor of 0.50 and 0.57 lower than the DOAS data, consistent with the toluene data. Given the nearly factor of 2 average difference between the DOAS and PTR-MS data, the analysis highlights the issue of representative sampling in an urban environment. Spatial concentration gradients complicate the sampling of hydrocarbons and likely other pollutants in urban areas for comparison with photochemical models.

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**Table 1.** Species measured at CENICA for intercomparison.

| PTR-MS (ion) | DOAS | Canisters GC-FID |
|---|---|---|
| Benzene (79) | Benzene | Benzene |
| Toluene (93) | Toluene | Toluene |
| $\sum$ $C_2$-alkylbenzenes[a] (107) | $\sum$ $C_2$-alkylbenzenes[d] | $\sum$ $C_2$-alkylbenzenes[a,e] |
| $\sum$ $C_3$-alkylbenzenes[b] (121) | Styrene | $\sum$ $C_3$-alkylbenzenes[f] |
| Styrene (105) | Phenol | Styrene |
| Phenol (95) | p-cresol | |
| Cresols[c] (109) | | |

[a] includes xylene isomers, ethylbenzene, and benzaldehyde

[b] includes all $C_9H_{12}$ isomers

[c] includes all cresol isomers

[d] calculated from measurements of p-xylene, m-xylene, and ethylbenzene (see text)

[e] includes xylene isomers and ethylbenzene

[f] includes all $C_9H_{12}$ isomers except 1,2,3-trimethylbenzene and isopropylbenzene

**Table 2.** Linear regressions fit parameters to GC-FID data.

| Species | Slope | Intercept (ppbv) | *r* | # Data points |
|---|---|---|---|---|
| PTR-MS regressions | | | | |
| Benzene | 0.95±0.06 | 1.1±0.13 | 0.646 | 35 |
| Toluene | 1.06±0.06 | 0.46±0.34 | 0.657 | 31 |
| $\sum$ $C_2$-alkylbenzenes | 1.10±0.07 | −0.20±0.23 | 0.614 | 31 |
| $\sum$ $C_3$-alkylbenzenes | 1.17±0.07 | 0.09±0.15 | 0.631 | 23 |
| DOAS regressions | | | | |
| Benzene | 0.84±0.05 | 0.84±0.09 | 0.478 | 36 |
| Toluene | 0.98±0.04 | 2.20±0.22 | 0.364 | 33 |
| $\sum$ $C_2$-alkylbenzenes | 1.39±0.07 | 2.04±0.32 | 0.344 | 29 |

Table 3. PTR-MS versus DOAS regressions fit parameters from prepared mixtures.

| Species | Slope | Intercept (ppbv) | Data range UV/Vis (ppbv) |
|---|---|---|---|
| Benzene | 0.95±0.02 | −29±9.4 | 173–651 |
| Toluene | 1.09±0.02 | −11±3.5 | 64–321 |
| Phenol | 0.96±0.04 | −6.1±3 | 15–71 |
| p-Xylene | 0.97±0.02 | −16±3 | 63–171 |
| Styrene | 1.16±0.08 | −29±10 | 78–212 |
| Ethylbenzene | 0.96±0.01 | −23±3 | 207–563 |
| 1,2,4-Trimethylbenzene | 1.08±0.03 | −12±3 | 50–135 |
| Naphthalene | 1.73±0.04 | −15±3 | 18–95 |

**Table 4.** PTR-MS versus DOAS regression fits parameters to ambient data.

| | Weighted monovariate fit | | | Weighted bivariate fit | | |
|---|---|---|---|---|---|---|
| | Slope | Intercept | *r* | Slope | Intercept | Excluded data |
| Benzene | 1.22±0.01 | 0.39±0.01 | 0.614 | 1.02±0.04 | 0.45±0.13 | DOAS<0.7 |
| Toluene | 0.60±0.003 | 0.81±0.03 | 0.554 | 0.63±0.002 | 0.93±0.05 | |
| $C_2$-alkylbenzenes | 0.59±0.002 | 0.04±0.01 | 0.583 | 0.48±0.004 | 0.84±0.06 | DOAS<1 |
| Naphthalene | 0.91±0.002 | −0.03±0.001 | 0.537 | 0.60±0.83 | 0.03±0.32 | |
| Styrene | 0.72±0.01 | 0.05±0.003 | 0.612 | | | DOAS<0.1 |
| Cresols | 1.06±0.01 | 0.01±0.01 | 0.557 | | | DOAS<0.01 |
| Phenol | 0.80±0.01 | 0.06±0.001 | 0.533 | 0.68±1.0 | 0.09±0.32 | DOAS<0.02 |

**Table 5.** Log-normal fit parameters to histograms of PTR-MS to DOAS data ratios.

| Species | PTR-MS/DOAS ratio<br>Mean | <br>$\sigma$ |
|---|---|---|
| Benzene | 1.14 | 0.281 |
| Toluene | 0.62 | 0.299 |
| $C_2$-alkylbenzenes | 0.50 | 0.296 |
| Naphthalene | 0.57 | 0.490 |
| Styrene | 0.77 | 0.317 |
| Cresols | 0.88 | 0.327 |
| Phenol | 1.49 | 0.403 |

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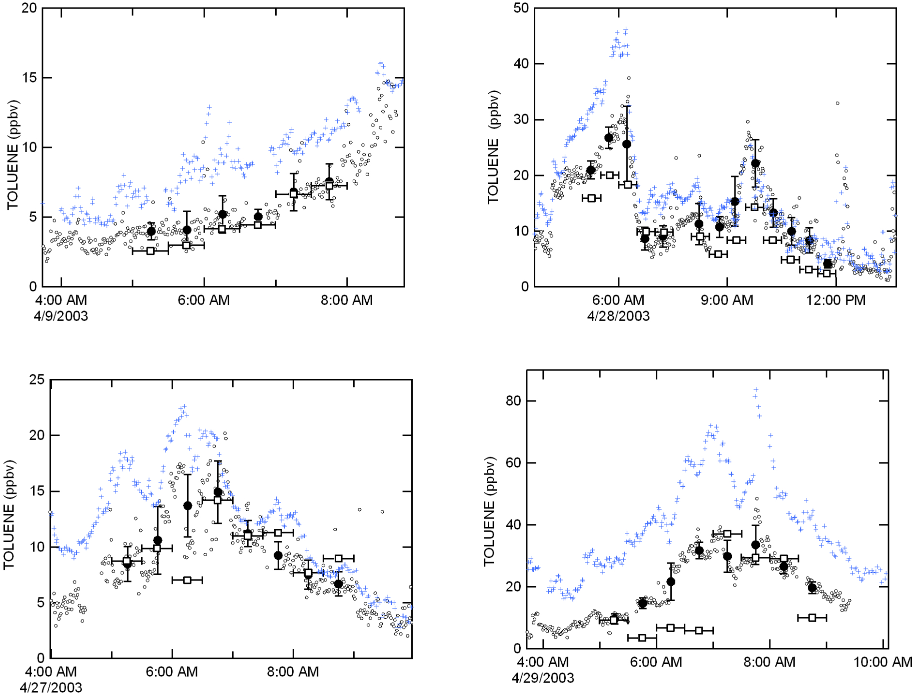

**Fig. 1.** Time series of toluene measurements made by the PTR-MS (small circles), DOAS (blue cross), canister GC-FID (open squares), and PTR-MS data averaged over the canister fill time (filled circles). Error bars on the canister data represent the fill time range.

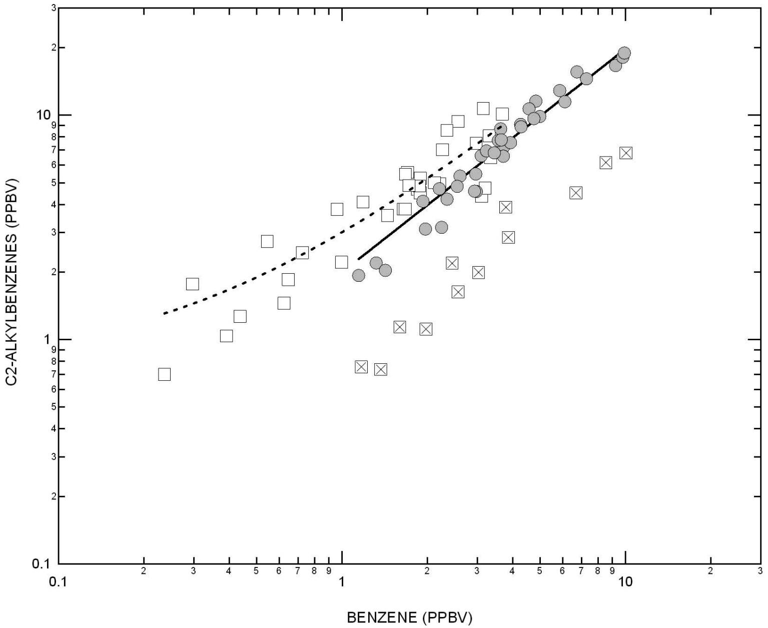

**Fig. 2.** $C_2$-alkylbenzenes versus benzene relationship for PTR-MS data (circles) and GC-FID data (squares) illustrating the outlying nature of several canister samples collected on 28 and 29 April indicated by crossed square symbols. The solid line is the linear regression fit through the PTR-MS data and the dashed lines is the linear regression fits through the GC-FID data excluding the 28 and 29 April outliers.

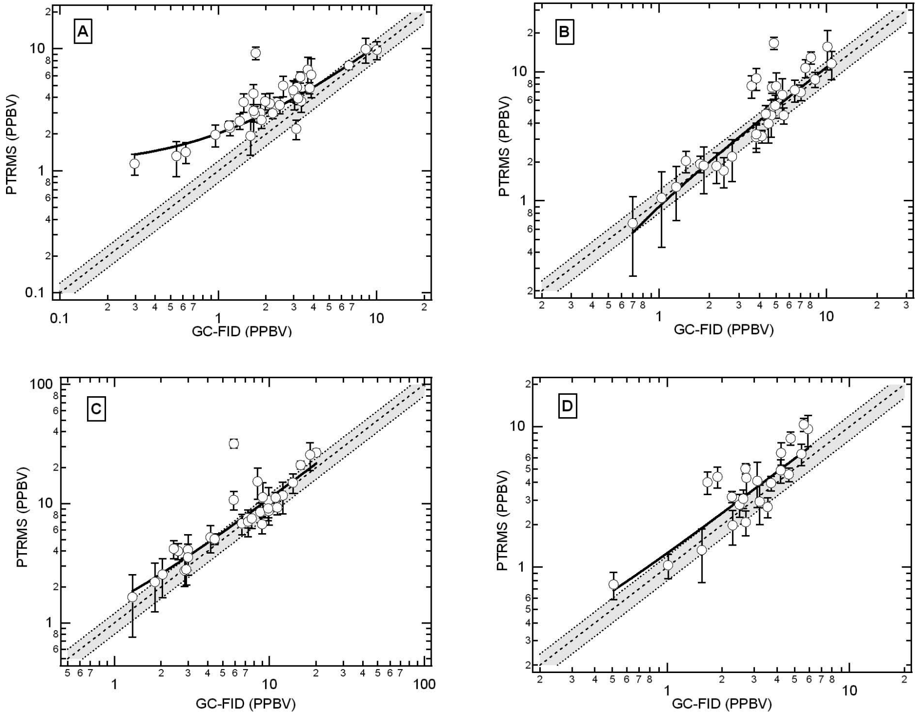

**Fig. 3.** PTR-MS versus GC-FID: **(a)** benzene **(b)** $C_2$-alkylbenzenes **(c)** toluene **(d)** $C_3$-alkylbenzene isomers. Regression fits are indicated by the solid black line. Dashed line is the 1:1 line bounded by ±20% range (grey shading).

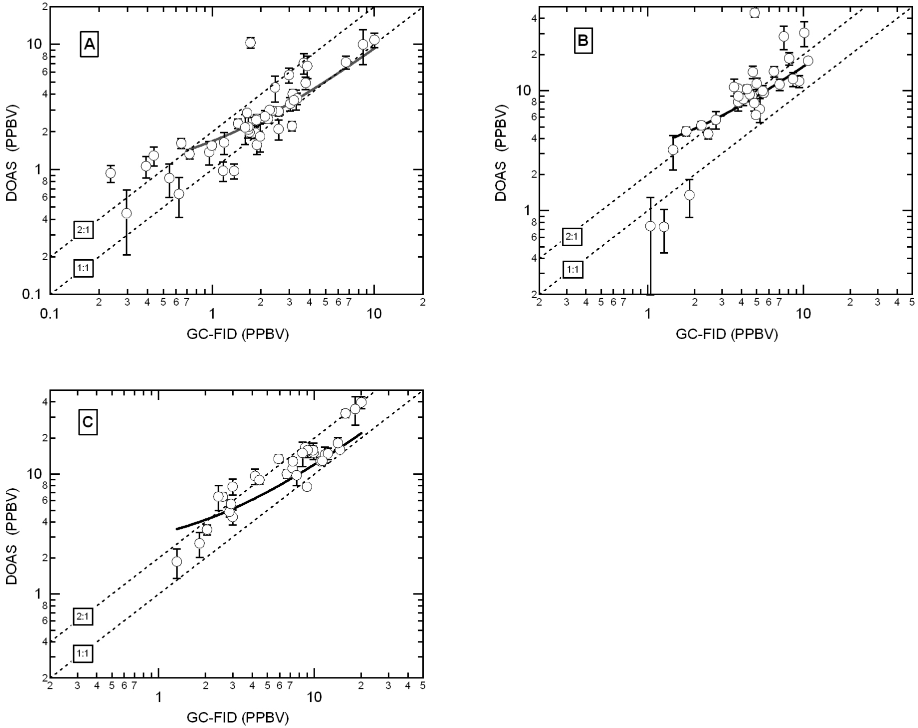

**Fig. 4.** DOAS versus GC-FID: **(a)** benzene **(b)** $C_2$-alkylbenzenes **(c)** toluene. Regression fit to the data is given by the solid black line. Dashed lines show slopes of 2:1 or 1:1 as noted.

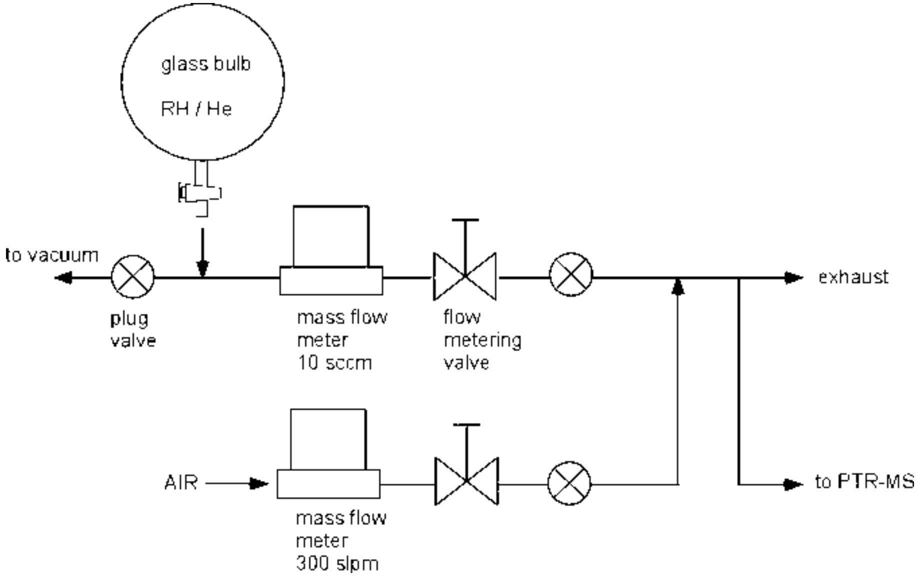

**Fig. 5.** Schematic of the dynamic dilution system used to dilute the glass bulb mixtures for measurement by the PTR-MS instrument. A quartz cuevette could be filled from the glass bulb to determine aromatic concentration in the bulb by UV/Vis absorption spectrometry. Lines were heat traced from the bulb to the PTR-MS.

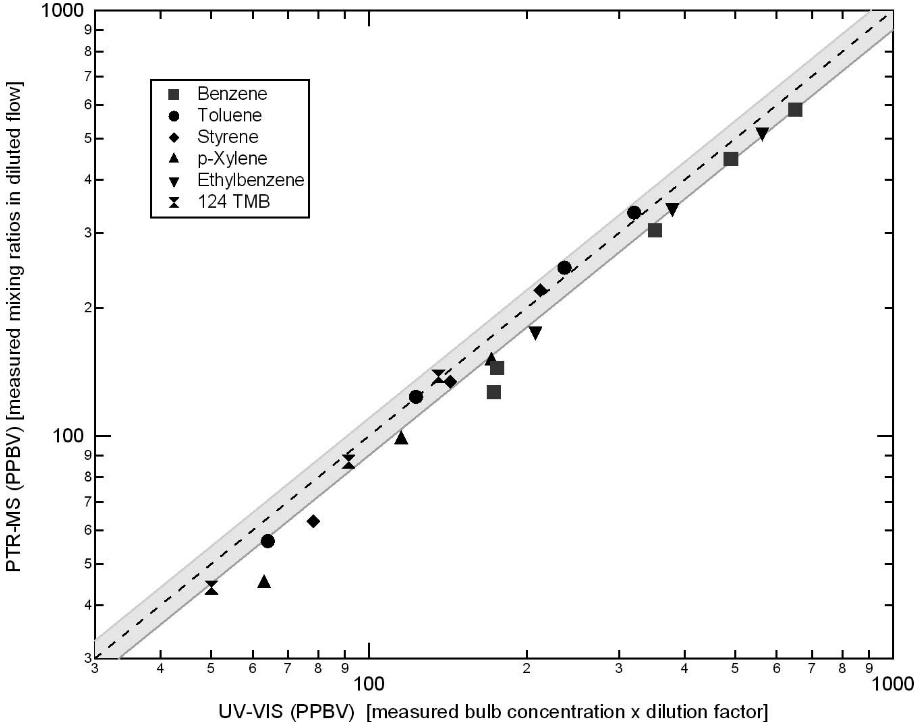

**Fig. 6.** Results from sampling prepared gas mixtures of aromatic species to evaluate the respective calibrations of the PTR-MS and DOAS instruments. Dashed line is the 1:1 line bounded by ±10% range (grey shading).

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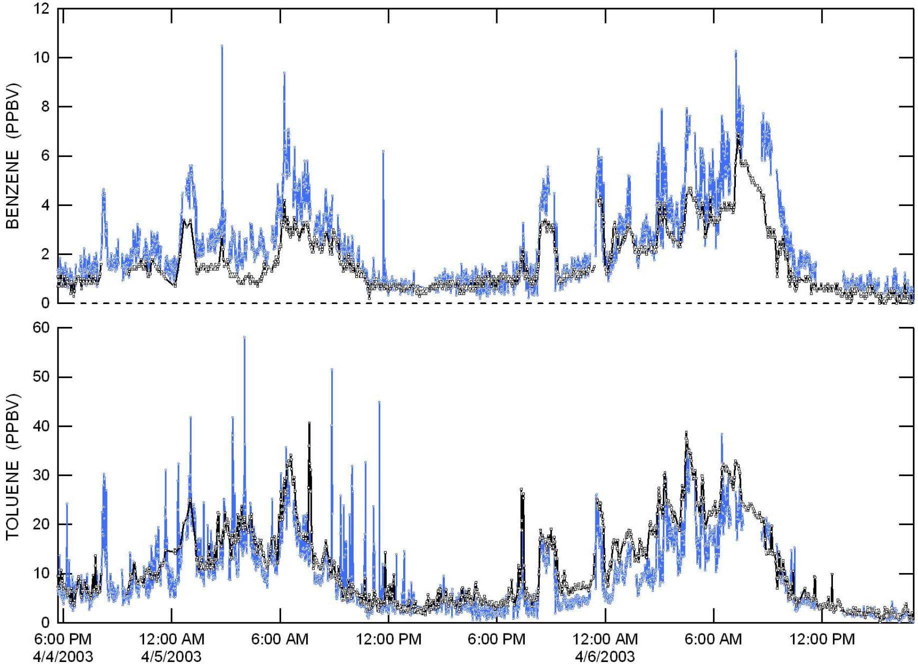

**Fig. 7.** Time series of PTR-MS (blue trace) and DOAS based measurements (black trace) of benzene (upper panel) and toluene (lower panel). The data show remarkable agreement on relatively small time scales.

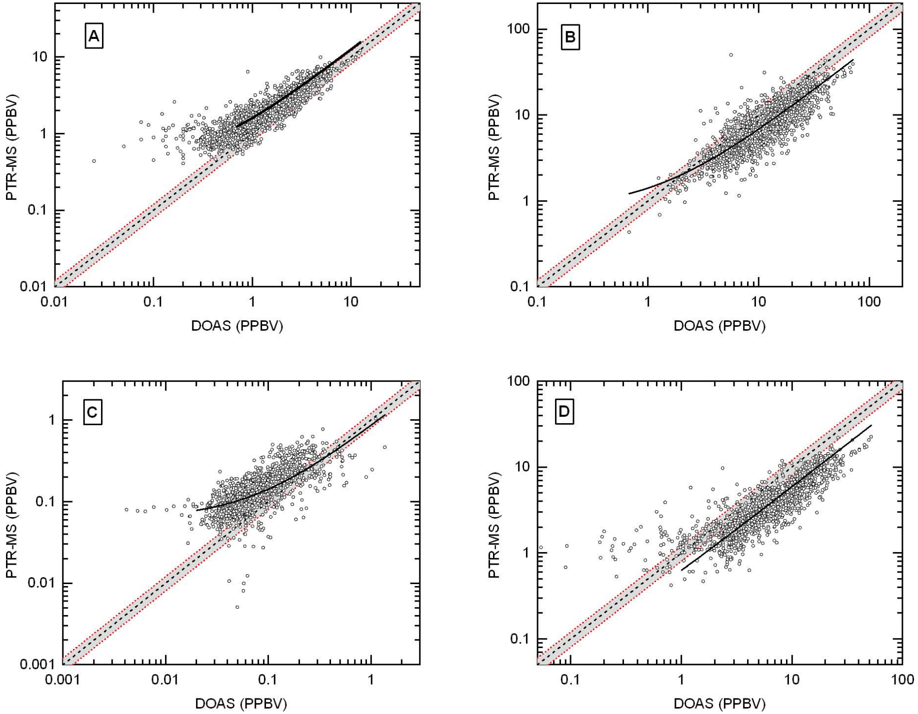

**Fig. 8.** PTR-MS versus DOAS **(a)** benzene **(b)** toluene **(c)** phenol **(d)** $C_2$-alkylbenzens. Plotted are 10 min averaged data. Monovariate linear regression fits are indicated by the solid black line. Dashed line is the 1:1 line bounded by ±20% range (grey shading).

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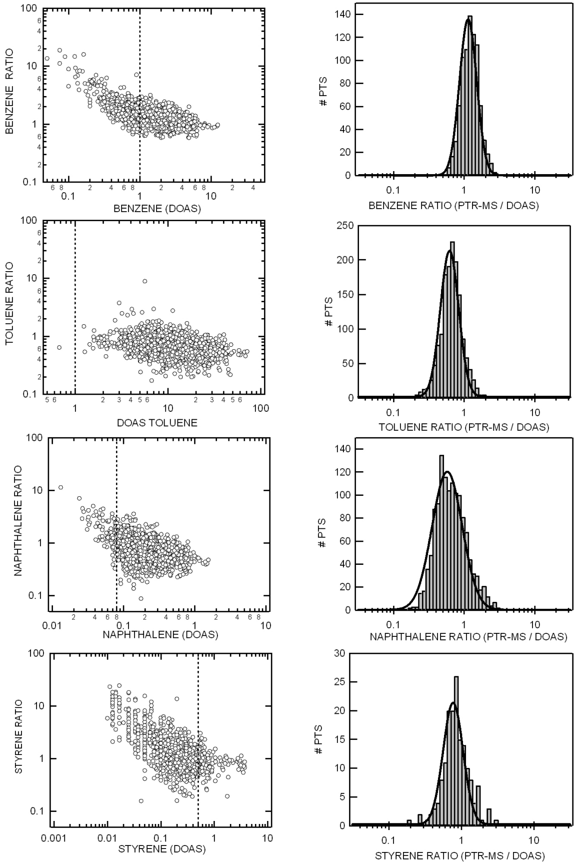

**Fig. 9.** The panels on the left display the PTR-MS to DOAS ratio versus DOAS for 10 min average data. The dashed line indicates the DOAS detection limit. The panels on the right display the corresponding histograms of the PTR-MS/DOAS ratio for those data were DOAS measurements were above the detection limit. The histogram plots were fit with a log-normal distribution curve (solid line).

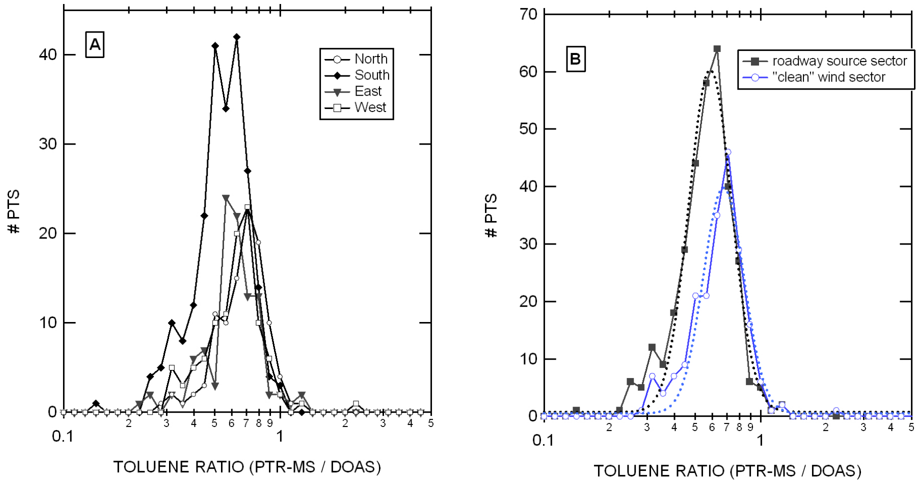

**Fig. 10.** Panel **(a)** shows frequency distributions of the ratio of the PTR-MS to DOAS toluene measurements sorted according to wind direction. Data are 1/2 h averages. In panel **(b)** south and east wind sector data from panel (a) were combined as roadway source sector, north and west wind sector data were combined and plotted as "clean" sector data. Dashed lines are fits to the respective histograms.