

Formaldehyde levels in downtown Mexico City during 2003

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Abstract

In this study, two spectroscopic techniques and two DNPH-sampling techniques were operated simultaneously in a downtown site of Mexico City to accurately determine formaldehyde levels during February and October of 2003. 1-hour samples from DNPH-silica cartridges and 4-h samples with an annular denuder system were collected during 4 days. The results are compared with the continuous data provided by an open-path Fourier transform infrared spectrometer (OP-FTIR) and a differential optical absorption spectrometer (DOAS) along a 426 m trajectory. Both spectroscopic techniques showed an agreement of 15% or less and a correlation coefficient of 0.86. The cartridge results presented average deviations relative to the OP-FTIR between –32% and 24% for the specific time periods but showed a clear similarity in the temporal patterns from the 5-min spectroscopic data. The results from the annular denuder samples show more limited precision (–35–65%) but the overall accuracy, when all data collected for the two 4-h periods was averaged, fell within a $\pm 15\%$ deviation range. This sampling configuration allowed to estimate an amount of formaldehyde in the particulate matter ($<2.5 \mu\text{m}$) of about 20% from that found in the gas-phase. Monthly average concentrations ranged between 23.9 ppb during February and 12.7 ppb during October of 2003. A 35% decrease in the average-peak values between the dry and wet seasons was identified.

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1. Introduction

Quantitative determinations of formaldehyde in the air are not only important from the health perspective but also from the role it plays in atmospheric chemistry (Carlier et al., 1986; Finlayson-Pitts and Pitts, 2000). HCHO constitutes the most abundant carbonyl in ambient air, having its origins both from direct emissions and photochemical reactions, generally through the oxidation of hydrocarbons in the presence of nitrogen oxides. This reactive compound, with a

lifetime of a few hours, is lost primarily from daytime photolysis below 360 nm and by its oxidation with OH radicals. Thus, by influencing the OH budget through these two main mechanisms, formaldehyde represents an important indicator of atmospheric reactivity and can act as precursor to organic aerosol formation in urban air (Grosjean, 1982).

A large number of techniques exist to measure HCHO in the gas-phase. The most common being the conversion of carbonyls to stable hydrazones when trapped in dinitrophenyl hydrazine (DNPH)-coated substrates (Shriner and Fuson, 1964). The hydrazones can then be separated chromatographically and detected through their absorption in the UV. Different versions of this derivatization technique involve unique sampler designs

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and sorbent types. Among the advantages of using these methods are the convenience and ease in setting them up, the decent sensitivities also for the larger carbonyls and that they are relatively inexpensive.

The spectroscopic techniques, on the other hand, are favored in the sense that are reliable and specific for HCHO, are not as subtle to interferences and collection efficiencies and are capable to provide real-time continuous data. First spectroscopic detection of HCHO in ambient air was achieved with a Fourier transform infrared spectrometer (FTIR) in a ~ 1 km multi-pass cell (Tuazon et al., 1978; Tuazon et al., 1981). Subsequent developments were able to reduce the detection limits into the sub-ppb regime with the differential optical absorption spectrometer (DOAS) method (Platt et al., 1979; Stutz and Platt, 1997) and in a matrix isolation experiment through infrared analysis (Griffith and Schuster, 1987). Later, the laser technology allowed for more compact and portable instruments to be constructed (Harris et al., 1989; Schiff et al., 1994). Recent developments using tunable diode laser absorption spectroscopy (TDLAS) allow for highly sensitive ground-based measurements of HCHO presenting replicate precisions of 0.040–0.056 ppb with a 5-min integration period (Fried et al., 1997), and have been successfully deployed in airborne field campaigns (Wert et al., 2003).

Several intercomparison studies have been made in order to evaluate the agreement between a number of DNPH samplers and the spectroscopic techniques (Kleindienst et al., 1988). In a laboratory and field investigation (Sirju and Shepson, 1995), two cartridge types coated with DNPH were evaluated against the TDLAS technique. As was found in a previous study (Arnts and Tejada, 1989), negative interferences with O_3 were observed in the DNPH-silica gel cartages. Generally, DNPH samplers arbitrarily differ from the TDLAS measurement in absolute values but have shown similar variations (Gilpin et al., 1997). An intercomparison between DNPH-coated denuders and DOAS was also carried out (Possanzini and Di Palo, 1999) and although the values correlated linearly, the scatter was about 30%.

Previous formaldehyde measurements in Mexico City between March and April of 1993 using DNPH-coated microimpingers, have reported mean values above 40 ppb during the 10–12 h sampling period and a maximum value observed at 110 ppb (Báez et al., 1995). In that contribution the formaldehyde concentrations were reported to be 2–3 times more abundant than acetaldehyde. In a more extensive study (Báez et al., 2000), evidence that the average concentrations of HCHO have decreased since 1993 was presented. Other investigations were done within this megacity to evaluate different sites (Báez et al., 2001) and HCHO exposures in indoor environments (Báez et al., 2003). In

general, the indoor concentrations were significantly higher than the corresponding outdoor measurements. Mean indoor/outdoor ratios ranged between 1.4 and 4.4.

In the present study, two derivatization and two optical remote sensing techniques were simultaneously employed to accurately determine the formaldehyde levels in Mexico City. Four days of sampling with DNPH-silica cartridges (DSC) and an annular denuder system (ADS) were carried out along with continuous open-path FTIR and DOAS measurements along a 426 m optical path. The results are intercompared and the data from the longer data set, acquired with the DOAS instrument from February to October of 2003, is reported.

2. Experimental

The measurements were done in downtown Mexico City, next to a station from the local network for atmospheric monitoring (RAMA) known as “Merced”. This urban site ($19^{\circ}24'N$, $99^{\circ}7'W$, 2250 m asl) has several avenues, parking lots and some green areas and can be characterized by having intense vehicular and commercial activity. Both the open-path FTIR and the DOAS instruments were installed on top of two four-storey buildings along the 426 m path, approximately 20 m above the surface. The infrared and UV beams, respectively, were traveling parallel to each other in the east–west direction. The RAMA monitoring station is located approx. 30 m away to the north from the west-end of the optical trajectories and is only ~ 8 m above the surface. The ADS samplers were installed at this site to give continuation to measurements done on other years whereas the DSC samplers were located next to the telescopes on top of the four-storey building.

Although not far from each other, the ADS measurements may present stronger local influences than the DSC samplers since the former was lower and closer to the avenue adjacent to the RAMA monitoring station. Also, taking into account the vicinity of the four-storey building to the ADS samplers and the RAMA station, one could expect that this physical barrier may prevent the instruments to capture the pollution during events with southerly winds. Nevertheless, comparisons of the ozone and CO timeseries acquired by the RAMA station and the OP-FTIR reveal that the location of the RAMA station reproduces reasonably well the ambient concentrations from the more representative, path-integrated determinations. The meteorological parameters are taken from a tower from the monitoring station which rises 25 m above the surface. A description of the measurement set-up and site has been presented in more detail elsewhere (Grutter et al., 2003).

2.1. Derivatization techniques

The first sampling system uses DSC. The downstream end of the cartridge (Waters, 1994) was connected to a calibrated flow meter. Air was passed through the cartridge at a flow rate of 1 L min^{-1} at 1-h time intervals from 8:00 to 18:00 h LST (sample volumes of 60 L). An ozone scrubber was connected upstream to the cartridge to avoid degradation of the hydrazone derivatives. Each cartridge was sealed with Teflon caps immediately after sampling, then wrapped in aluminum foil and refrigerated.

The ADS consists of the following components in order with the air flow: a PM_{2.5} cyclone (URG, Chapel Hill, NC) which removes particles larger than $2.5 \mu\text{m}$ at a flow of 10 L min^{-1} ; a three concentric glass annular denuder (URG, 150 mm long with 1 mm gaps) coated with a 10% KI solution to remove O_3 (Parmar and Grosjean, 1990); and two three concentric annular denuders (URG, 242 mm long with 1 mm gaps) with a 5 mL acidic solution (0.5% H_3PO_4) of 2,4-dinitrophenylhydrazine (Acros) at 1% for the collection of carbonyl compounds. Additionally, a 3-stage filter compartment holding a porous Teflon membrane (Gellman Science, Ann Arbor, MI), $1 \mu\text{m}$ porous size and 47 mm in diameter, was located between both the DNPH denuders. This configuration was chosen in order to obtain a simultaneous characterization in the gas-phase (1st DNPH denuder), as is commonly done, and to establish the amount of carbonyls in the particulate matter (filter plus 2nd denuder), as proposed by Andraca-Ayala and Ruiz-Suárez, (2004).

The chemical analysis of all samples from both sampling systems was performed in the same manner. The samples were eluted with 10 mL of HPLC grade acetonitrile and $20 \mu\text{L}$ aliquots were injected into a Perkin Elmer (Isocratic pump, Norwalk, CT) liquid chromatograph. The analytical conditions were as follows: a Spherisorb S5 ODS2 reverse phase analytical column, water/acetonitrile 45/55 v/v as a mobile phase and a flow rate of 1 mL min^{-1} . The derivatives were detected at 360 nm with a UV/vis detector (GBC, LC 1200) and the calibration was performed with direct injection of standard mixtures of known amounts of hydrazones dissolved in acetonitrile. These standard mixtures gave a linear response up to 50 ppm of the corresponding hydrazones, corresponding to $767 \mu\text{g m}^{-3}$ of formaldehyde.

DSC laboratory blanks and cartridge field controls were analyzed to determine background levels of DNPH derivatives. The average HCHO concentration and standard deviation of cartridge laboratory blanks was $0.47 \pm 0.30 \mu\text{g}$ per cartridge. The levels in cartridge field controls were similar to the laboratory blanks. The analytical detection limit for the formaldehyde derivative was $1.32 \mu\text{g m}^{-3}$ for a sample volume of 60 L at STP.

The cartridge collection efficiency was determined by connecting two cartridges in series, giving $>95\%$ at the sampling conditions above mentioned. The sample breakthrough of the cartridges is 500 ppbv considering the combined concentrations of all carbonyls when 120 L of air is sampled.

Field blank levels in annular denuders (ADS) is equivalent to a 4 h average concentration of $0.006 \mu\text{g m}^{-3}$ when sampling at 10 L min^{-1} . In the Teflon filter field blanks, levels were equivalent to $0.03 \mu\text{g m}^{-3}$. The geometry of the denuders is highly efficient to trap all gas phase HCHO in the air sample even at very low relative humidity. This is paramount when assigning all HCHO found in the backup denuder to that degassed from the Teflon filter. With ample use, the sampling coating tends to adhere to the glass walls making the denuders to loose some efficiency. Although the overall sampling efficiency remains sufficient when this happens, an adequate distinction between formaldehyde in the gas-phase and in PM_{2.5} becomes problematic.

2.2. Spectroscopic techniques

The spectroscopic determination of HCHO in the infrared was achieved with an open-path FTIR system. Working in a bistatic configuration, this remote sensing technique consists of sending a modulated infrared beam horizontally across the atmosphere and collecting it with a pair of Cassegrain telescopes (polished aluminum, 30 cm in diameter). The interferometer at the transmitting end is a Nicolet (Nexus 460, Madison WI) bench equipped with a ZnSe beamsplitter operated at 0.5 cm^{-1} resolution. The liquid-nitrogen-cooled MCT detector at the receiving end permits, with the existing optics, a working range of $600\text{--}4000 \text{ cm}^{-1}$. The signal is transmitted back to the spectrometer via a cable for process and analysis. The instrument was constructed by Industrial Monitor and Control Corp. (Austin, TX) and has been described more thoroughly by Grutter et al. (2003). The $2776\text{--}2782 \text{ cm}^{-1}$ spectral window was used for the quantification of formaldehyde using a least-squares regression algorithm and a HITRAN generated spectrum (Rothman et al., 1998) as reference. The minimum detection limit at 426 m is estimated to be 4 ppb or better, and the uncertainties resulting from the residuals in the retrieval process oscillated between 10% and 20%.

Formaldehyde concentrations were also monitored during a longer period of time with a commercial DOAS system (Opsis, model AR500). This instrument consists of a xenon light source located at the east-end of the 426 m trajectory (next to the FTIR receiver telescope) and a collimating mirror. At the receiving end, a Newtonian telescope coupled to an optical fiber collects the radiation and transmits it into the opto-analyzer. The instrument was reference-calibrated using

a laboratory optical bench for defining a background transmission spectrum and wavelength-calibrated with a low-pressure mercury lamp. The quantitative analysis was performed by the instruments' internal software (Opsis, 1995), and the concentrations were corrected for the local temperature and pressure conditions. Although not specified by the producer, the detection limit of HCHO at this optical path-length was comparable to the OP-FTIR, i.e. 3–4 ppb, and the uncertainties generated during the evaluation process typically fell in the 8–18% range.

3. Results

As can be observed from Figs. 1 and 2, formaldehyde concentrations were measured simultaneously with the DSC, the ADS and the open-path FTIR spectrometer during 4 days in a downtown site of Mexico City. The continuous line represents the FTIR data with a 5 min resolution. The steps with the thick line correspond to 1-h sample results from the DSCs and the bars denote the two 4-h sample collection periods with the ADS. The light gray portion of the bar represents the gas-phase

portion of formaldehyde while the dark gray is the amount of HCHO found in the particulate matter (Section 2.1).

In general, there is a good agreement between the spectroscopic and both derivatization methods. One- and 4-hour FTIR averages together with the corresponding DSC and ADS data, respectively, are presented in Table 1. The percent deviation for each sampling period relative to the FTIR data is presented in the third column of each day. There is a consistent underestimation of HCHO in the morning hours by the DSC sampler, which can be probably attributed to a moisture and temperature effect. The KI-coated coils deployed for O₃ scrubbing could be condensating a significant amount of formaldehyde (and water vapor) hindering the flow of this gas into the cartridge. In the following sampling hours, the deviations are less consistent and the DSC results clearly show a similar behavior as the FTIR trend. The ambient temperature range registered during the 08–09 time span was 13.0–16.5 °C, whereas during the next hour it increased to 16.5–18.5 °C. The negative deviations observed predominately between 13 and 14h, when the ozone peaks, suggest that there might be a slight interference

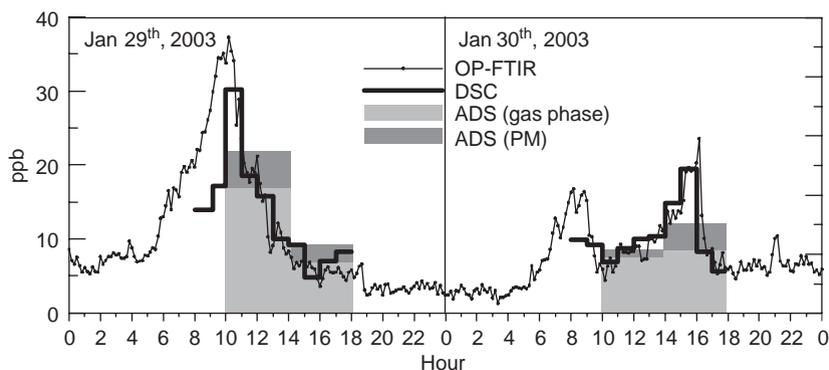


Fig. 1. Comparison of HCHO results from the OP-FTIR continuous data, DSC and ADS for the 29th and 30th of January, 2003.

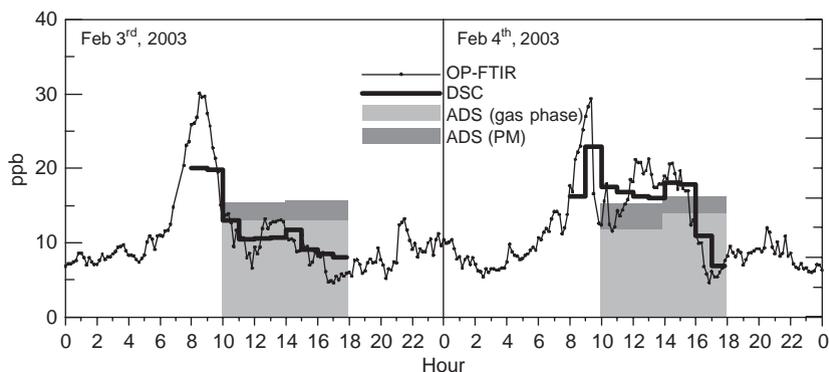


Fig. 2. Comparison of HCHO results from the OP-FTIR continuous data, DSC and ADS for the 3rd and 4th of February, 2003.

Table 1
FTIR averages, 1-hour DSC and 4-hour ADS results in ppb for the specified time spans and dates

Time span	29 January 2003			30 January 2003			3 February 2003			4 February 2003			Avg. dev (%)
	OP-FTIR	DSC	% Dev.										
08–09	23.13	13.90	–40	15.58	9.88	–37	28.05	19.99	–29	21.03	16.21	–23	–32
09–10	32.22	17.16	–47	9.30	9.17	–1	21.98	19.80	–10	21.05	22.97	9	–12
10–11	32.48	30.17	–7	5.97	6.85	15	12.42	13.03	5	13.68	17.51	28	10
11–12	19.85	18.54	–7	8.35	8.71	4	9.35	10.48	12	15.30	16.80	10	5
12–13	14.70	15.78	7	8.00	10.02	25	10.72	10.60	–1	20.00	16.20	–19	3
13–14	9.90	9.95	1	10.55	10.36	–2	12.85	10.70	–17	18.53	16.05	–13	–8
14–15	7.00	9.15	31	13.08	14.79	13	10.05	11.76	17	19.23	18.06	–6	14
15–16	6.12	4.80	–22	17.68	19.45	10	8.82	9.11	3	16.08	17.87	11	1
16–17	5.18	7.06	36	13.87	8.32	–40	6.78	8.55	26	8.03	10.96	36	15
17–18	5.38	8.30	54	6.92	5.57	–19	5.38	8.02	49	6.18	6.89	11	24
	OP-FTIR	ADS	% Dev.										
10–14	19.23	16.97	–12	8.22	7.48	–9	11.33	13.04	15	16.88	11.89	–30	–9
14–18	5.90	6.76	15	12.89	8.34	–35	7.76	12.98	67	12.38	13.90	12	15

The deviations of the cartridge and denuder data is in percent relative to the OP-FTIR value.

from this oxidant (see conclusions). However, the average deviations throughout the day are found to be less consistent and oscillate between –32% and 24%.

The deviations for the ADS with respect to the OP-FTIR fell in the –35–67% range (Table 1) on individual cases, but were within 15% when the sampling periods were averaged throughout the study. As was stated in Section 2, the site where the ADS sampler was located was closer to the ground with respect to the DSC sampler and the spectroscopic measurements. Correlations attempting to establish a relationship between the sign and magnitude of the deviations with respect to wind direction were not conclusive in order to entirely explain the results. However, the negative deviations corresponded mainly to the NE quadrant, the direction which is more open and free of large perturbations from buildings and which also has several sport facilities and parks. The positive values correspond to NW and SE wind directions and are thought to be influenced by more local sources such as the large avenue located a few meters to the west from the monitoring station. Moreover, there was a general tendency in the deviations observed from both derivatization techniques to rise towards positive values with increasing wind speeds.

The amount of formaldehyde in PM_{2.5} taken as the sum of this compound found in the filter and in the 2nd denuder (Section 2.1), is represented by the dark areas in Figs. 1 and 2. This corresponds to an average and standard deviation of $20 \pm 6\%$ from the gas-phase values throughout the campaign. Andraca-Ayala and Ruiz-Suárez (2004) consider the 0.2 particle/gas-phase ratio as a conservative threshold above which an appropriate phase distribution will no longer be convincing. In order to accurately establish the phase distribution in the

ADS, the denuders need to have the highest trapping efficiency as in the case of brand new denuders. The ones deployed did not fit that requirement as they were used in a series of experiments carried out in the city. However, at a gas-phase/PM_{2.5} ratio of 0.20, the ADS setup is still highly efficient to trap all HCHO in both gas and suspended phases and thus the present results suggest a significant amount of formaldehyde in the particulates.

Since the largest data set for this study was provided by the DOAS instrument, it was necessary to compare the results obtained from this technique and the open-path FTIR which was installed parallel to it for a more limited time. As an example, the timeseries obtained during 6 days of continuous monitoring from both of these spectroscopic techniques is presented in Fig. 3. The data shown have been averaged every hour in order to simplify the comparison and display. In this plot, one can observe that the general trend is being coherently followed by both techniques explained by a coefficient of determination (R^2) of 0.86. The linear fit obtained from the correlation (inset in Fig. 4), however, reveals that the DOAS values are approximately 11% higher than the OP-FTIR.

In Table 2 the results from the continuous data acquired with the DOAS instrument between February and October of 2003 is presented. Ozone and carbon monoxide from the RAMA monitoring station are also reported to characterize the pollution degree of the investigated air volumes. The monthly averages (third column) show that the formaldehyde concentrations drop considerably from 8.9 ppb in February to 5.1 ppb in May. A maximum value of >30 ppb, however, is registered at least once a month until June, which is the

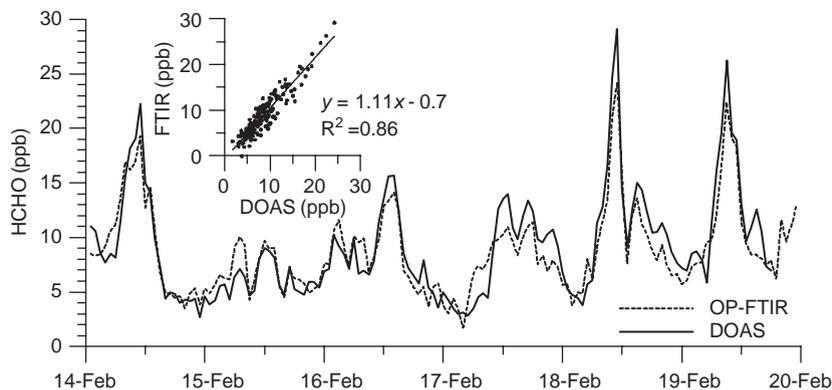


Fig. 3. Time series of formaldehyde (ppb) during 6 days in 2003 obtained from the OP-FTIR and DOAS instruments along a 426 m path. In the inset, the 1-h averages are plotted correlating these two techniques.

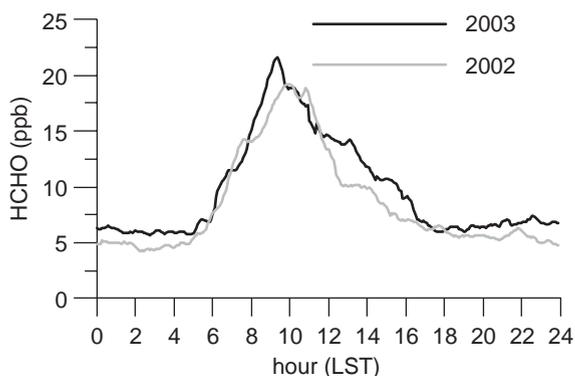


Fig. 4. Diurnal patterns of formaldehyde from a 2-week period in February of 2002 and 2003 obtained with the OP-FTIR instrument.

month when the rainy season starts. The average of maxima observed every day (second column) decreases from 23.9 ppb in February to 18.0 ppb in June, and after this month the levels revert to a base value of $\sim 13.5 \pm 0.8$ ppb all through October.

Since the open-path FTIR experiment was carried out in two consecutive years at the same site, it was possible to compare the formaldehyde concentrations during the first 2 weeks of February from 2002 to 2003. As can be observed from Fig. 4, there is no significant difference in the behavior and levels of HCHO measured. The maximum appears between 9 and 10 a.m. averaging just above 20 ppb as was shown in Table 2 for this particular month.

4. Conclusions

Reliable measurements of HCHO are needed to understand the relationship between the species involved

in photochemical processes and to refine the models. Also, it is important to investigate the contribution from primary emissions which are known to originate from motor vehicles (Anderson et al., 1996; Zweidinger et al., 1988).

In this study, a wealth of information is provided with respect to the formaldehyde levels in Mexico City. It has been possible to assess on the quality of the data acquired more commonly with the DNPH samplers, and to intercompare two spectroscopic remote sensing techniques. Generally, a good agreement between the derivatization techniques and the spectroscopic open-path measurements has been obtained. The DSC 1-hour data followed the temporal variability of HCHO quite well with respect to the OP-FTIR, except for the early morning hours. There is a good possibility that the KI-coated copper coil deployed for the removal of ozone could be hindering the flow of the carbonyls when the temperature is below 15 °C or so. Also, there seems to be a slight tendency for the deviation of the DSC-samples relative to the OP-FTIR value to become positive when the ozone is low and negative when the ozone is high. This behavior was evaluated for the 12–16 h data when the temperature and relative humidity remained between 22–24 °C and 30–40%, respectively, and does not totally explain the –32–24% deviation range observed for all data. Other effects which are probably more important have to do with local variations since one is a point-sample measurement and the other a long-path integration.

Although the amounts of gas-phase HCHO detected in the ADS samples presented deviations from –35% to 65%, the averages of all data from the two sampling periods fell within 15% from the spectroscopic values (see Table 1). Some but not all of the deviations could be explained from wind correlations, where local sources could be directly affecting the location of this sampler more vigorously since it was located closer to the ground

Table 2
HCHO monthly maxima, peak averages and monthly averages from February to October 2003

2003	HCHO (ppb)			CO (ppm)		OZONE (ppb)	
	Max value	Avg. max	Avg ^a	Avg. max	Avg	Avg. max	Avg
February	35.0	23.9	8.9±4.6	4.77	1.83	110	30
March	34.8	22.7	7.5±4.9	5.05	1.97	92	26
April	38.8	20.9	6.0±4.7	5.07	2.27	110	32
May	37.7	18.8	5.1±4.5	3.44	1.86	79	34
June	33.9	18.0	7.1±3.7	4.08	2.13	78	23
July	20.1	13.6	4.3±3.6	3.64	1.59	86	24
August	22.2	14.0	4.8±3.6	3.51	1.74	96	27
September	24.8	14.3	5.3±4.0	3.88	1.80	84	23
October	21.8	12.7	4.9±3.6	3.46	1.58	63	18

Average peak maxima and monthly averages are also given for CO and O₃ for reference.

^aGaussian distribution averages and standard deviations from monthly histograms.

with respect to the other instruments. The sum of the HCHO detected in the filter and in the second DNPH-denuder suggests that there is a considerable amount of lightly bound HCHO in particles smaller than 2.5 μm. The average of the eight samples analyzed for particulates <2.5 μm, represented by the dark gray areas in Figs. 1 and 2, corresponds to 20% of the formaldehyde found in the gas-phase. Some caution needs to be taken with this result since it is strongly dependant on the physical state of the denuder and thus its trapping efficiency. There is, nevertheless, strong evidence that high concentrations of this toxic pollutant are present in the smaller particles thus having a considerable implication on human health.

From the comparison between DOAS and OP-FTIR techniques, their absolute agreement was found to fall within 15% and a correlation coefficient of 0.86 could be determined. Both of these methods are attractive tools for monitoring formaldehyde in the sense that real-time, high-resolution and continuous data can be obtained. Additionally, the path-integrated measurement provides with a more representative evaluation of the air pollution levels when compared to point samplers.

The daily maxima were observed mainly in the 09–11 h (LST) time period and their monthly averages ranged between 23.9 ppb during February and 12.7 ppb during October. Two main patterns were identified during 2003, one corresponding to the dry season, when monthly average-maxima fell in the 18–24 ppb range (February–June) and the rainy season, for which average values in the 13–14 ppb range were obtained (July–October). This represents a 35% decrease of the formaldehyde levels between the dry and wet periods. Monthly averages of this gas in the 4–9 ppb range are considered high but not surprising for this urban site where daily peaks of carbon monoxide and ozone often exceed levels of 5 ppm and 100 ppb, respectively. The

current results are also indicative that although there has been a significant reduction in the formaldehyde levels since the early 1990s (Báez et al., 1995), measures to further decrease the exposures of this toxic pollutant are still required.

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