

**Evaluation of UV
ozone monitors**

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Technical note: Evaluation of standard ultraviolet absorption ozone monitors in a polluted urban environment

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Abstract

The performance of the EPA Federal Equivalent Method (FEM) technique for monitoring ambient concentrations of O₃ via ultraviolet absorption (UV) has been evaluated using data from the Mexico City Metropolitan Area (MCMA-2003) field campaign.

5 Comparisons of UV O₃ monitors with open path Differential Optical Absorption Spectroscopy (DOAS) and open path Fourier Transform Infrared (FTIR) spectroscopy instruments in two locations revealed average discrepancies in the measured concentrations of +13% to -10%. Excellent agreement of two separate open path DOAS measurements at one location indicated that spatial and temporal inhomogeneities were not
10 substantially influencing comparisons of the point sampling and open path instruments. The poor agreement between the UV O₃ monitors and the open path instruments was attributed to incorrect calibration factors for the UV monitors, although interferences could not be completely ruled out. Applying a linear correction to these calibration factors results in excellent agreement of the UV O₃ monitors with the co-located open path
15 measurements; regression slopes were 0.94 to 1.04 and associated R² values were >0.89. A third UV O₃ monitor suffered from large spurious interferences, which were attributed to extinction of UV radiation within the monitor by fine particles (<0.2 μm) due to a particulate filter with too large a pore size. The overall performance of this particular monitor was poor owing to a combination of interferences from a contaminated
20 particle filter and/or ozone scrubber. Suggestions for improved operation practices of these UV O₃ monitors and recommendations for future testing are made.

1 Introduction

Ozone (O₃) often serves as the benchmark for the overall pollution level of a given airshed and has been designated as a “criteria pollutant” by the United States Environmental Protection Agency (US EPA). The costs of reducing O₃ pollution are estimated
25 in the billions of dollars (Leston et al., 2005). For example, a report by the Instituto

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Nacional de Ecología (INE) in Mexico (McKinley et al., 2003) found that the implementation of several control measures could achieve a 3% reduction in daily maximum ozone concentration at the cost of approximately two billion dollars. Regulatory action is initiated by the US EPA when measured O₃ concentrations in an urban area exceed a certain threshold (see Reynolds et al., 2004, for recent discussion of one-hour and eight-hour averaged daily maxima standards); this is referred to as “non-attainment”. Hundreds of US counties are either close to the threshold or already in non-attainment, and it has been suggested that up to half of the non-attainment counties in the US have O₃ concentrations in excess of the threshold as a result of measurement interferences (Leston et al., 2005).

The improvement of monitoring of O₃ and its precursors was mandated by the 1990 Clean Air Act Amendments (Sect. 182 (c) (1)) (Demerjian, 2000). The US EPA has developed recommendations for standard measurement techniques and calibration practices (Environmental Protection Agency, 1998; Paur and McElroy, 1979) to ensure the quality of measurements for these pollutants. The Federal Reference Method (FRM) for O₃ is a chemiluminescence detector, however, by far the most common technique for determining the ambient concentration of O₃ is ultra-violet absorption (UV O₃ monitor), which has been designated as a Federal Equivalent Method (FEM). Indeed, UV O₃ monitors account for almost all of the UV monitoring in the US (Leston et al., 2005). Monitoring networks in other countries have also adopted UV O₃ monitors making them the most ubiquitous instruments for O₃ monitoring worldwide. Due to the importance of measuring O₃ and the widespread use of UV O₃ monitors, it is critical that this measurement technique be accurate, precise, and well-characterized.

The technique of UV absorption measurement of O₃ has been described elsewhere (Proffitt and McLaughlin, 1983) and only a brief description is included here. Advantages of the UV absorption technique include its relatively low cost and overall reliability. UV O₃ monitors employ mercury (Hg) lamps as reliable sources of line UV radiation at 253.65 nm, corresponding closely to the peak in the O₃ cross section (Sander et al., 2002). A typical UV O₃ monitor utilizes an ozone-specific scrubber, often manganese

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dioxide (MnO_2) on a substrate or heated silver wool, to create an ozone-free air flow for reference. The UV radiation intensity passing through this reference flow is compared to that through a flow of ambient air and the number density of O_3 is determined by the straight-forward Beer-Lambert absorption equation. The measurement of the O_3 number density by this absorption method is in principle an absolute determination, relying only on the absorption cross section of the O_3 molecule at 253.65 nm. Scattering or absorption of UV radiation by ambient aerosols is prevented by a PTFE fluorocarbon particle filter with pore sizes between 0.2 and $5.0 \mu\text{m}$ placed in the inlet to the UV O_3 monitor. These filters must be changed frequently to prevent a buildup of materials which might then catalyze the breakdown of O_3 on the filter or release compounds that could absorb UV radiation. Although UV absorption is in theory an absolute measurement technique, in practice, these monitors are routinely calibrated by generating a known amount of O_3 via UV photolysis of molecular oxygen in dried/clean air, often ambient air passed through a desiccant and a charcoal filter.

Possible interferences in this measurement technique have been summarized in several recent reviews (Cavanagh and Verkouteren, 2001; Demerjian, 2000; Environmental Protection Agency, 1993; McClenny et al., 2002; Parrish and Fehsenfeld, 2000; Sickles, 1992). Overall, previous evaluations of the performance of UV O_3 monitors have yielded mixed results. Several studies have shown adequate performance of UV O_3 monitors in comparison to chemiluminescence (Ryerson et al., 1998) and spectroscopic (Stevens et al., 1993) instruments. Alternatively, a number of studies have shown interferences due to scattering of UV radiation by fine particles within the instrument (Arshinov et al., 2002; Leston and Ollison, 2000) and anomalous sensitivity of the manganese dioxide scrubbers to ambient water vapor, causing a discrepancy compared with calibrations typically performed with dry gas (ASTM, 2003; Butcher and Ruff, 1971; Cavanagh and Verkouteren, 2001; Leston et al., 2005; Maddy, 1999; Parrish and Fehsenfeld, 2000). Aromatic hydrocarbons and oxidized or nitrated aromatics are known to absorb UV radiation and are the most likely to be present in sufficient quantities in an urban environment to potentially contribute to this type of interfer-

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ence (Cavanagh and Verkouteren, 2001; Grosjean and Harrison, 1985; Hudgens et al., 1994; Kleindienst et al., 1993; Leston et al., 2005). Overall, there is still a need for field intercomparisons of these UV O₃ monitors, particularly intercomparisons done in urban locations with high O₃ concentrations typical of non-attainment conditions (Parish and Fehsenfeld, 2000).

This study aims to evaluate the performance of several standard UV O₃ monitors during a field measurement campaign in Mexico City during spring of 2003. The Mexico City Metropolitan Area field campaign (MCMA-2003) featured a comprehensive suite of both gas and particle phase instrumentation from numerous international laboratories, including multiple measurements of O₃. We utilize this unique data set to assess the performance of these standard monitors in a heavily polluted urban atmosphere, examine possible interferences and make recommendations for advances in testing and operation of these monitors that should be pursued.

2 Measurements

Figure 1 provides a map of the MCMA with the locations of the various sites from where measurements will be presented. A more complete description of the MCMA-2003 field campaign is given elsewhere (de Foy et al., 2005; Molina and Molina, 2005). Details of the O₃ measurements made at each location are described below, and we briefly introduce the sites here. “CENICA”, where the campaign was headquartered, receives a mix of fresh pollution from nearby traffic corridors and aged pollution from more downtown locations. The “La Merced” site is located very near a busy roadway and the La Merced marketplace. The “Pedregal” site is located at an elementary school in an affluent residential neighborhood west of the city center. As a downwind receptor site, Pedregal often has the highest ozone readings in the city. The “Santa Ana” site is located in the small town of Santa Ana just outside of Mexico City to the southwest and up on a mountain ridge above the Mexico City basin floor. Mexico City is surrounded on three sides by mountains (east, south and west); Santa Ana is close to the southern

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gap in the mountains at Amecameca and receives mostly aged urban air during the day and rural air overnight. The ozone data measured by various instruments located at these sites form the basis of this evaluation.

2.1 CENICA

5 The “supersite” for the MCMA-2003 campaign was located at the headquarters building of the Centro Nacional de Investigacion y Capacitacion Ambiental (CENICA) and included a comprehensive suite of both gas phase and aerosol instrumentation from a number of Mexican, American and European institutions (de Foy et al., 2005; Molina and Molina, 2005). The two-story CENICA building is located on the Iztapalapa campus of the Universidad Autónoma Metropolitana (UAM), to the southeast of the city center (see Fig. 1). The site is approximately 1000 m from a minor roadway and 1500 m from a major roadway. For the MCMA-2003 campaign, two research grade long path Differential Optical Absorption Spectroscopy (DOAS) instruments and a research grade long path Fourier Transform Infrared (FTIR) spectrometer were installed on the rooftop of the CENICA building and were operated by groups from the Massachusetts Institute for Technology (MIT) and Chalmers University of Technology (CTH), respectively. 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. For the MCMA-2003 campaign, the DOAS-1 light path was directed towards an antenna tower in a south-easterly direction at an average height of 16 m with a 430 m path length (total 860 m). The DOAS-2 lightpath was directed towards a local hill side of Cerro de la Estrella in a south-westerly direction at an average height of 70 m with a 2.21 km path length (total 4.42 km). Both LP-DOAS instruments measured O₃ among other species (Volkamer et al., 1998, 2005b) using ozone’s unique specific narrow-band (<5 nm) absorption structures between 252–262 nm (DOAS-1) and 325–358 nm (DOAS-2). Temperature dependent absorption

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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 (Fayt and van Roozendaal, 2001; Stutz and Platt, 1996). The detection limits for O₃ were 1.3 ppb for DOAS-1 and 5.0 ppb for DOAS-2. This significantly smaller detection limit of DOAS-1 reflects the roughly 20 times larger differential absorption cross section in the wavelength range used by this system. This potential for much more sensitive ozone measurements is partly offset by increasing light extinction from Rayleigh and Mie scattering at shorter wavelengths, which limits attainable absorption pathlengths and thus detection limits. Also, the broadband light absorption from O₃ in the Hartley band reduces the transparency of the atmosphere and may increase photon shot-noise in the spectra. Moreover, different straylight sources gain relative importance in this wavelength range, and need to be corrected for. Finally, the atmospheric oxygen absorption features in the Herzberg band-systems need to be eliminated carefully to allow for absolute measurements of ozone by DOAS. We have overcome all the above limitations following the procedure described in Volkamer et al. (1998).

The open-path FTIR system was operated parallel to the DOAS-1 lightpath sampling nearly identical airmasses (same length light path, <2 m apart). The FTIR consisted of a medium resolution (1 cm⁻¹) spectrometer (Bomem MB104) coupled to a homemade transmitting and receiving telescope, and provided CO data (among other species) with 5 min integration time. Spectra were analyzed using the latest HITRAN database cross sections (Rothman et al., 2003) and a nonlinear fitting algorithm (Samuelsson et al., 2005¹). The detection limit for the FTIR system was 10 ppb.

In addition to the equipment installed for the MCMA-2003 campaign, CENICA maintains a monitoring station located on the roof of its headquarters building, which includes a standard UV O₃ monitor (Advanced Pollution Instruments (API) model #400, detection limit 3 ppb, heated metal wool scrubber (12 W) with typical operating temper-

¹Samuelsson, J., Galle, B., and Mellqvist, J.: Personal communication, 2005.

ature of 70°C). The inlet for this monitoring station was 15 m above the ground. This UV O₃ monitor was calibrated on the same afternoon and via the same standard method as the one on board the ARI Mobile Lab (see Sect. 2.3).

2.2 La Merced, Pedregal and Santa Ana

5 Another featured component of the MCMA-2003 campaign was a measurement site located downtown near the La Merced marketplace; the site is located in close proximity to a busy roadway and <500 m from major bus station (TAPO). This site and instrumentation have been described in detail elsewhere (Grutter et al., 2003); briefly, researchers from Universidad Nacional Autónoma de México (UNAM) operated two
10 open path remote sensing instruments: one research grade FTIR and one commercial DOAS system (Opsis AR500). The light paths were run side-by-side between the rooftops of two four-story buildings (~20 m above the ground) and were 426 m long. O₃ was measured by both FTIR and DOAS in addition to numerous other compounds; the detection limit for O₃ by the FTIR technique was better than 2 ppb (Grutter et al., 2003) and employs the latest HITRAN database cross sections (Rothman et al., 2003). The
15 UNAM instruments were in close proximity (<30 m) to a monitoring station operated by Red Automática de Monitoreo Ambiental (RAMA, 2005). RAMA operates 32 monitoring sites around the Mexico City metropolitan area, 20 of which are equipped with standard UV O₃ monitors, including the La Merced location (API 400, MnO₂ scrubber). The RAMA network has been audited by the US EPA (Environmental Protection Agency, 2003), and was concluded to be “accurate and well-implemented”. In particular, the O₃ audit data “were of outstanding quality with no significant bias or imprecision detected across all stations and concentrations audited.” The inlet at the La Merced site is ~6 m above the ground and is <10 m from the nearby roadway.

25 The Pedregal site also housed a RAMA monitoring station including a UV O₃ monitor (API 400, MnO₂ scrubber). The inlet for the monitoring station is at a height of ~4 m and the site is ~300 m away from a major roadway. At the Santa Ana site, researchers from CENICA operated a monitoring station that included several criteria pollutant monitors

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including a UV O₃ monitor (Thermo Environmental (TECO), Model 49C with a MnO₂ scrubber). The Santa Ana monitoring station was 600 m away from a minor roadway with an inlet that was 3 m above the ground.

2.3 Aerodyne Mobile Laboratory

Another major component of the MCMA-2003 campaign was the Aerodyne Research, Inc. Mobile Laboratory (ARI Mobile Lab), a van equipped with a comprehensive suite of research grade gas and particle phase instrumentation (Kolb et al., 2004), including a UV O₃ monitor (Thermo Environmental (TECO), Model 49-003 with an unheated MnO₂ scrubber). All instruments included in this study sampled from the main inlet line. When moving, this inlet sampled from in the front of the mobile lab at a height of 2.4 m above the road surface, protruding 1.2 m from the front bulkhead above the driver seat, resulting in a typical minimum horizontal distance between the inlet and a chased vehicle of at least several meters (Shorter et al., 2005). While stationary, an extension was added to the inlet to sample from a height of 5 m above the ground. Measured and calculated lag times for all instruments were short (<10 s) and agreed within 15% (Herndon et al., 2005).

The ARI Mobile Lab was operated in two modes interspersed throughout the five weeks of the MCMA-2003 field campaign – mobile and stationary modes (Kolb et al., 2004). The goals of the mobile mode were to follow specific vehicles to measure their on-road emission ratios and to map out the influence of stationary emission sources. In stationary mode, the ARI Mobile Lab visited the three locations within Mexico City listed in Sect. 2.2 and made continuous measurements at each location for several days in a row. Additionally, the ARI Mobile Lab spent a majority of the nights and several full days during the five week field campaign in the parking lot adjacent to the CENICA building (Sect. 2.1).

The UV O₃ monitor on board the ARI Mobile Lab was calibrated near the beginning of the field campaign via the EPA standard method by RAMA technicians for continuity of comparisons with RAMA monitors, as all UV O₃ monitors in the RAMA network are

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routinely calibrated by this method (RAMA, 2005). This calibration procedure involved the use of a charcoal filter for the production of O₃ free air in which a known amount of O₃ is generated by the photolysis of O₂ at 185 nm. The performance of the O₃ generator was tracked by the use of a reference O₃ monitor maintained in pristine condition in a laboratory. Additionally for the ARI Mobile Lab UV O₃ monitor, zero checks were performed several times throughout the campaign by placing a charcoal filter in front of inlet to remove ambient O₃; the resulting readings were always near zero (between -4 and 2 ppb). The detection limit for this UV O₃ monitor was 2 ppb.

3 Results and discussion

3.1 Interference from ambient particles for UV O₃ monitor on board ARI Mobile Lab

During the course of the five week MCMA-2003 campaign, distinct “spike events” in the UV O₃ monitor on board the ARI Mobile Lab were observed when the ARI Mobile Lab was sampling the ambient diluted exhaust from on-road diesel vehicles. This UV O₃ monitor registered spikes of up to 400 ppb occurring simultaneously with large increases in CO₂ and NO concentrations from sampled combustion plumes. Figure 2 shows an example of such an O₃ spike event while sampling a diesel truck with large particle loadings, but then not present during a chase of a non-diesel microbus just minutes later. More than twenty-five of these events were observed during the MCMA-2003 campaign. All such interference events were coincident with large enhancements in particle number density. Almost all of these events were observed when the ARI Mobile Lab was clearly sampling the exhaust from a diesel vehicle (Canagaratna et al., 2004; Herndon et al., 2005; Shorter et al., 2005). Of the various instruments on board the ARI Mobile Lab, the best correlations in time for these interferences were found with several particle instruments, specifically a DustTrack PM_{2.5} instrument, which measured the mass loading of particulate matter smaller than 2.5 microns, and an EcoChem Polycyclic Aromatic Hydrocarbon (PAH) monitor, which measured signal response to

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photoionization of particulate surfaces and has been shown to respond strongly to surface bound PAHs and possibly to elemental carbon (EC); see Marr et al. (2004) and Jiang et al. (2005) for a description of the use and interpretation of these instruments while sampling very fresh on-road exhaust emissions. Also on board the ARI Mobile Lab, an Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000) measured size resolved chemical composition of non-refractory particles less than $1\ \mu\text{m}$. The AMS showed an increased loading of organic material from diesel vehicles, but no enhancement in nitrate, sulfate or ammonium, consistent with other observed diesel exhaust measurements (Canagaratna et al., 2004). Poor correlations at the time of these O_3 interference spikes were found with other gas phase species measured on board the ARI Mobile Lab, including CO, formaldehyde (HCHO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and a suite of volatile organic compounds (VOC) measured in real time by an on-board Proton Transfer Reaction Mass Spectrometer (PTRMS) (Knighton et al., 2006).

Diesel vehicles are not known to emit O_3 directly (Chow, 2001; Yanowitz et al., 2000). The NO concentrations observed in Fig. 2 (>500 ppb) result in a short lifetime for O_3 with respect to loss via reaction with NO (<6 s); this was shorter than the residence time in the inlet for the UV O_3 monitor inside the ARI Mobile Lab (~ 12 s). Thus, if O_3 were directly emitted by a diesel vehicle, it would have to be in enormous concentrations (>2 ppm per 1 ppm of CO_2 emitted) to be observed in the large concentrations in Fig. 2. It is concluded that these large O_3 spikes were not due to O_3 itself, but rather are due to interferences in the O_3 measurement.

Diesel vehicles are known to emit particles with large number densities in both a nanomode, ($0\text{--}0.05\ \mu\text{m}$), and an accumulation mode, ($0.05\text{--}0.5\ \mu\text{m}$) (Canagaratna et al., 2004; Kittelson, 1998). Particles less than $0.2\ \mu\text{m}$ in geometric diameter are known to pass through standard inlet filters and cause a interferences in UV O_3 monitors, by as much as a factor of three in a previous study (Arshinov et al., 2002), although not all studies have observed this (Huntzicker and Johnson, 1979). Submicron particles, which were emitted from diesel vehicles and pass through the particulate filter of the

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UV O₃ monitor and scatter and/or absorb UV light within the detection chamber, were thus the most likely explanation for the large interferences like that shown in Fig. 2. Other gas phase species emitted from diesel vehicles, but not measured by the ARI Mobile Lab, or species desorbing off of the particulate filter specifically during sampling of diesel exhaust could also explain these observed interferences. However, neither of these possibilities seems as likely as an interference from submicron particles entering the detection chamber within the UV O₃ monitor.

The question is whether this type of interference presents a significant issue for most UV O₃ monitors. Arshinov et al. (2002) observed a significant interference to a UV O₃ monitor from fine particles with median particle diameters between 0.06 to 0.07 μm. When a suitable filter to remove these particles was placed in front of the UV O₃ monitor, the interference disappeared. Obviously, the UV O₃ monitor on board the ARI Mobile Lab in this study did not have a filter with a small enough pore size to remove these fine particles. This is not necessarily the case for all UV O₃ monitors however. Additionally, the placement of UV O₃ monitors in locations that do not directly sample fresh traffic emissions allows the fine particles characteristic of fresh traffic emissions to grow into large enough sizes to be more efficiently filtered out. Thus, sampling done from the ARI Mobile Lab represented an extreme case, with particle loadings often greater than 2000 μg m⁻³, which were heavily dominated by fresh traffic emissions and were thus comprised mostly of fine particles (D_p < 0.2 μm). The interference in the UV O₃ monitor on board the ARI Mobile Lab roughly correlated with the PM_{2.5} particle loading as measured by the DustTrack instrument; the correlation factor was (0.12–0.18 ppb) of O₃ interference per 1 μg m⁻³ of particle loading. Ambient loadings typical for many urban environments of < 15 μg m⁻³ would thus lead to a potential interference for a normally situated UV O₃ monitor (at least one that was not on board a mobile laboratory) of < 3 ppb. Over the course of an eight hour day in an urban area with a daily maximum O₃ concentration of 100 ppb, this type of interference could lead to an average measured O₃ concentration that is at most 3% higher than reality. The actual influence of fine particles on the measured O₃ concentration by typical UV O₃ moni-

tors would be expected to be even less owing to a more suitable placement of most UV O₃ monitors that will not sample primarily fresh traffic emissions. This indicates that this type of interference is not likely to be a significant problem, even for UV O₃ monitors that do not use a filter with a small enough pore size to remove fine particles (D_p < 0.2 μm). In summary, although the UV O₃ monitor on board the ARI Mobile Lab was shown to have large interferences from fine particles, this type of interference is not likely to greatly affect most UV O₃ monitors used for ambient sampling.

3.2 Overall comparison of multiple O₃ measurement techniques

During MCMA-2003, O₃ concentrations in Mexico City were observed to exceed 200 ppb on several occasions and exceeded 100 ppb on every day of the 5 week campaign. Thus, the evaluation of the UV O₃ monitors in this setting constituted a test under non-attainment conditions by the US EPA's standards. In this study, the performance of UV O₃ monitors at the CENICA and La Merced sites was evaluated by comparison with co-located DOAS and FTIR open path spectroscopic measurements, which are both non-intrusive and are considered absolute techniques in so far as they rely on extensively studied absorption cross sections (Orphal and Chance, 2003). Table 1a lists the results of linear regressions for the O₃ concentrations as measured by UV O₃ monitors versus those from the corresponding spectroscopic measurements. The two UV instruments differed from the open path measurements by more than 8% at each of the CENICA and La Merced sites, however one was systematically higher than the open path determination and the other was lower. The R² values listed in Table 1 are all >0.89. The three most probable reasons for divergence from near-perfect agreement were: (3.2.1) inherent difficulties in comparing open path and point sampling techniques, (3.2.2) incorrect calibration factors for the UV O₃ monitors, and (3.2.3) interferences in the UV O₃ monitors. The UV O₃ monitor on board the ARI Mobile Lab (Table 1d) is not included in this assessment for reasons described below in Sect. 3.2.4.

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3.2.1 Comparison of open path and point sampling measurements

The comparison of an open path measurement with a point sampling measurement is inherently difficult owing to the spatial and temporal inhomogeneities within an urban airshed, driven by complex micro-meteorology and/or strong vertical gradients in concentration due to dry deposition. At the CENICA site, the measurements made by the two open path DOAS instruments, which were pointed in different directions and measured at different mean heights and pathlengths, provide an insight into the uniformity of the air mass in the area surrounding the site. The high level of agreement between the two DOAS instruments shown in Table 1b (15 min averaged points, regression slope ≥ 0.93 , $R^2=0.96$) indicates that O_3 is mixed rather homogeneously over a spatial scale of few kilometers near the CENICA site. The regression slope for this comparison was less than unity (0.93) owing to a number of points at low O_3 concentrations where the DOAS-2 light path showed higher O_3 levels than the DOAS-1 light path, which is thought to be due to the closer proximity of the DOAS-1 light path to fresh combustion sources (see discussion below Sect. 3.2.2). Comparisons between the point sampling UV O_3 monitor and either of the DOAS instruments should be able to achieve the same level of agreement, but they do not.

To further put the comparisons of the O_3 measurements in context, we also compared the measurements of CO by point sampling and open path techniques at both the CENICA and La Merced sites; see Table 1c. Because CO is not as reactive as O_3 nor as likely to have strong vertical gradients owing to deposition (Stutz et al., 2004), CO should be more homogeneously mixed throughout the boundary layer within the city. At the same time, CO is a primary pollutant from mobile and other sources and there may be inhomogeneities in close proximity to CO sources that do not occur for O_3 . For example, the relatively poorer correlation of the CO monitor at the La Merced site may be due to the close proximity of the La Merced RAMA monitoring station to a heavily trafficked corridor. The R^2 values for the linear regressions for the CO measurements are thus another indicator of the level of spatial and temporal variation. The

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R^2 values for the CO measurements were smaller than those for the respective O_3 regression plots at both the CENICA and La Merced sites. This further corroborates our conclusion above that spatial inhomogeneities do not limit the comparison of open-path and point-sampling O_3 measurements at these two locations, particularly for the afternoon periods of elevated ozone concentrations. The next step is to examine why the slopes of the regression analyses deviate from unity.

3.2.2 Calibration factors for UV O_3 monitors

Barring interferences (discussed below in 3.2.3), the slopes of the regression analyses for these comparisons are indicative of the relative calibration factors. We again use the linear regressions for co-located open path DOAS O_3 and CO measurements as points of comparison with the O_3 measurements. The open path DOAS O_3 and CO regressions had slopes closer to unity than those for the O_3 regression plots, indicating better agreement in the relative calibration factors of the two instruments. The slopes for the open path DOAS O_3 and CO comparisons were all within 7% of unity. The slopes of the O_3 regression were not as consistent; (1.08–1.13) and (0.82–0.90) for CENICA and La Merced respectively. It is noteworthy, that differences were found largest for the commercial DOAS instrument at La Merced (–18%). The reason for this is unclear and unfortunately, any further discussion of this data is only possible to a very limited extent, as the evaluation procedure employed by the company is not clear to us. A previous comparison of the O_3 reported at La Merced by this DOAS and the more reliable FTIR instrument (Grutter and Flores, 2004), however, presented a very high correlation ($R^2=0.99$). Since the absolute concentration by the DOAS was consistently lower than that from the FTIR, a correction to the DOAS results was applied accordingly. For this reason, the regression comparing the O_3 monitor with the FTIR (–10%) is probably a better indicator of the actual difference. Intercepts for the O_3 regressions with respect to the UV monitors were negligible indicating that the differences in the regression slopes were not skewed by offsets, but are attributed to

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differences in the calibration factors. Because of the given evidence, the most probable reason for the discrepancies found is then determined to be due to the calibration factors in the UV O₃ monitors.

A closer inspection of the daily patterns corroborates that the calibration of the UV O₃ monitors was the cause of the non-unity slopes in the linear regression plots. Figure 3a shows that the UV O₃ monitor differs most in absolute concentration from the corresponding spectroscopic measurement at both CENICA and La Merced during afternoons when the O₃ concentrations were at their highest. Although the absolute concentration difference (Fig. 3b) varied throughout the course of the day, the percentage difference (Fig. 3c) remained constant from roughly 10 a.m. to 5 p.m. local time each day, with values around +12% ($\pm 2.5\%$) of the ambient O₃ concentration for CENICA and -14% ($\pm 8.4\%$) for La Merced. Overall, in both comparisons, the consistent percentage difference for most of the day light hours, averaged over the span of a month leads us to the conclusion that the UV O₃ monitors at both sites differed from the co-located open path measurements due to a calibration issue.

This discrepancy in the UV O₃ monitor calibration factors can be corrected for by multiplying the O₃ concentrations from the UV O₃ monitors by a constant factor based on the linear regression plots' slopes listed above. Such a correction brings all comparisons with all four open path measurements listed to within 5% with corresponding R² values all greater than 0.90; see Table 2. This is excellent agreement in light of the other comparisons shown in Table 1 and previous studies, which have concluded that UV O₃ monitors can measure tropospheric O₃ concentrations with uncertainties less than $\pm 3\%$ (Parrish and Fehsenfeld, 2000).

The open path spectroscopic measurements are dependent on knowledge of the absorption cross section for the molecule being detected. Recent studies have shown that the infrared cross sections of O₃ from the HITRAN data base, upon which the FTIR open path measurements depend, are up to 5% too large (Picquet-Varrault et al., 2005). Although using this information could bring the comparisons with the UV O₃ monitor into better agreement, it would only partially explain the observed differences

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of 10%.

In theory, the UV O₃ monitor is an absolute measurement that does not require adjustment. In practice, however, these monitors are routinely calibrated by generating a known amount of O₃ in a flow of dry zero air and then adjusting the “span” or relative response of the UV O₃ monitor to match the calibration standard (Parrish and Fehsenfeld, 2000). The US EPA recommends that calibrations be performed every six months with zero/span checks performed every two weeks with adjustments of the span up to 20% considered acceptable (Environmental Protection Agency, 1998). Typically, monitoring networks perform calibrations and zero/span checks more frequently, e.g. calibrations every month, and zero/span checks nightly (TCEQ, 2006). UV O₃ monitors in the RAMA monitoring network are calibrated every two weeks with span/zero checks performed weekly and allowable span adjustments of ±10% (RAMA, 2005). Some studies have shown problems in this method arising from the use of dry calibration gas where ambient measurements are made in moist air (Leston et al., 2005; Parrish and Fehsenfeld, 2000), and this is discussed in Sect. 3.2.3. The most likely explanation for the observed differences between the open path and UV O₃ monitors is the resetting of the calibration factors on the UV O₃ monitors as part of routine calibrations. We reiterate that the RAMA network has been audited by the US EPA (Environmental Protection Agency, 2003) and found to be operating well under the guidelines for proper maintenance of their instruments, which indicates that it was the approved calibration procedures that allowed these differences to occur.

Looking at the rest of the diurnal pattern for the O₃ comparisons in Fig. 3c, the largest percentage differences occur during the morning (5 a.m. to 9 a.m. local time), which we will refer to here as “morning rush hour”. During this period, the O₃ concentrations were at their smallest and, as such, were most prone to slight differences between open path and point sampling measurements, in particular the influence of NO and other combustion products. Motor vehicles are the most dominant NO_x sources in this environment, and at this time of day, the major source of O₃ at the surface is the down-mixing of O₃ from above. Typical NO concentrations during the morning rush hour were

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on order of >100 ppb, making the lifetime of O₃ with respect to titration by NO < 30 s. During the morning rush hour, the suppression of the O₃ concentration by 40% to 70% as measured by the UV O₃ monitor relative to the DOAS-2 open path at CENICA and relative to both open path instruments at La Merced was consistent with both of these UV O₃ monitors being in relatively close proximity to fresh NO emissions. Thus, O₃ as measured at these point sources was titrated by NO to a larger degree than along the open paths used by the spectroscopic techniques, which would have been more greatly influenced by down-mixing of O₃ from aloft. Note that the absolute differences in O₃ concentration during this morning rush hour time frame were 5 to 7 ppb for these three comparisons, which was only just larger than the combined uncertainties of the pairs of instruments. The relatively higher amount of O₃ measured by the UV O₃ monitor at CENICA relative to the DOAS-1 open path instrument requires a different explanation; this difference in the concentration of UV O₃ monitor minus DOAS-1 had a maximum of 170%, which corresponds to 3.4 ppb out of 1.9 ppb total O₃. We note that combustion sources also peak at this time of day; see Fig. 3d which shows the diurnally averaged profiles of CO at CENICA and La Merced. The higher concentration of O₃ as measured by the UV O₃ monitor could potentially be explained by a small interference, presumably from a combustion product, perhaps fine particles (Sect. 3.1). However, the magnitude of this difference (3.4 ppb) was within the combined uncertainty of the two measurements, so there was no definitive evidence for an interference in the UV O₃ monitor here.

3.2.3 Possible interferences in UV O₃ monitors

As introduced earlier, several, but not all, previous studies have observed interferences in the O₃ concentrations reported by UV O₃ monitors (Arshinov et al., 2002; Huntzicker and Johnson, 1979; Leston et al., 2005). The observed biases of the UV O₃ monitors at the two comparison sites in this study, positive at CENICA and negative at La Merced, indicate that a single type of interference in the UV O₃ monitor was not responsible for both of the observed differences between the monitors and the co-located open

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path instruments. However, we more thoroughly explore the possibility of interferences in the UV O₃ monitors from (a) changing ambient relative humidity levels affecting the adsorption rate of aromatic compounds onto the scrubber in the UV O₃ monitor (Leston et al., 2005) or directly influencing the transmission of UV radiation through the detection cell within the monitor (Wilson, 2005) and (c) particles entering the detection chamber of the monitor (described in Sect. 3.1) or contaminating the particle filter.

(a) We observed no evidence for either a positive or negative interference in the UV O₃ monitors from aromatic compounds being adsorbed/desorbed onto/from the scrubber coincident with variations in the ambient relative humidity. A positive interference in the UV O₃ monitor would be expected during periods when the ambient relative humidity was decreasing or relatively stable, which would be from approximately 8 a.m. to 5 p.m. local time as shown in Fig. 3d. A positive bias in the UV O₃ monitor was observed at the CENICA site during these times, however, the diurnal profiles for ambient relative humidity were similar at both the CENICA and La Merced sites, and as noted above, the biases in the UV O₃ monitors were of opposite direction relative to the co-located open path spectroscopic instruments.

A positive interference would also be expected during periods of high ambient concentrations of aromatic compounds which may adsorb onto the scrubber, causing an apparent increase in O₃ concentration (Huntzicker and Johnson, 1979). The MCMA-2003 field campaign included multiple measurements of ambient VOC compounds from several instruments: the two DOAS instruments located at the CENICA supersite, two PTRMS instruments, one of which was on board the ARI Mobile Lab (Knighton et al., 2006), and canister sampling followed by gas chromatography (GC) analysis at all of the locations described in this study (Lamb et al., 2004). These measurements provide a consistent picture that within Mexico City overall loadings of gas phase aromatics were higher during the morning hours (on order of ~30 ppbv) and lower during the afternoons (on order of ~15 ppbv). This was inconsistent with the overall pattern of the observed differences between the UV O₃ monitors and the open path instruments, which showed a maximum in the afternoon. Additionally, both the DOAS and

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PTRMS instruments located at the CENICA site observed several large styrene (up to 3.9 ppbv) and naphthalene (up to 1.9 ppbv) events during the five week field campaign (Volkamer et al., 2005a). Laboratory tests have shown that UV O₃ monitors respond to both styrene (Grosjean and Harrison, 1985; Hudgens et al., 1994) and naphthalene (Kleindienst et al., 1993), with response factors of (20%–113%) and 116%, respectively. Corresponding interferences in the UV O₃ monitors as compared to the DOAS instrument were not observed for these styrene and naphthalene events. We conclude that ambient aromatic hydrocarbons do not significantly influence the measurements made by UV O₃ monitors.

However, aromatic VOC's are considered less likely to be the primary compounds responsible for interferences in UV O₃ monitors than the oxidized and/or nitrated compounds formed from these aromatic VOC's. For example, an EPA laboratory study (Wisbith, 1999) showed that modest levels of o-nitrotoluene (24 ppb) can cause a significant interference at low humidity (20–30%). (This same study (Wisbith, 1999) also showed that mercury was a significant interference, but mercury was found only in sporadic short-duration events in Mexico City and would not have been the cause of interferences in the diurnal O₃ levels.) The aromatic hydrocarbon concentrations measured during this study were large enough such that the concentrations of oxidized and/or nitrated products of these aromatics, which were not directly identified by the VOC measurements made during MCMA-2003, might be found in sufficient concentrations to cause an interference as large as the observed difference between the UV O₃ monitors and the co-located spectroscopic instruments. Thus, measured hydrocarbon levels during MCMA-2003 provided no evidence for interferences in the UV O₃ monitors from oxidized and/or nitrated aromatic compounds, but did not definitively rule out the possibility.

A negative interference in the UV O₃ monitors would be expected as relative humidity rises in the late afternoon and aromatic compounds desorb from the scrubber into the reference channel of the UV O₃ monitor (Leston et al., 2005). However, the negative difference between the UV O₃ monitor and the open path spectroscopic instruments at

La Merced occurred during the early afternoon as relative humidity was decreasing.

Some field studies involving co-located measurements of O₃ via chemiluminescence and UV absorption on board an airplane have shown no evidence for this effect of ambient relative humidity variations on the scrubber performance (Ryerson et al., 1998).

5 However, careful laboratory studies have shown that variations in relative humidity can interact with the material of the detection cells within the UV O₃ monitors, causing spurious O₃ concentration differences during times of rapid changes in ambient relative humidity (Meyer et al., 1991; Wilson, 2005). In this study, the fastest change in ambient relative humidity occurred before 9 a.m. local time, which did not correspond with
10 the maximum observed difference between the UV O₃ monitors and the open path spectroscopic instruments which occurred several hours later, typically after 12 p.m. local time. Additionally, this afternoon time period of maximum discrepancy in the UV O₃ monitors was coincident with periods of relatively stable ambient relative humidity. Thus, we did not observe any evidence for this interference of changing relative
15 humidity in this field study.

Lastly, we note that our results contradict those of Leston et al. (2005) from their Mexico City study, who observed a difference between co-located UV and chemiluminescence O₃ monitors that they attributed to contamination of the O₃ scrubber in the UV O₃ monitor. The reasons for this contradiction are unclear, but further measurements are suggested at the end of this article.
20

In conclusion, we observed no evidence for any interference, either positive or negative, in the UV O₃ monitors from varying ambient relative humidity levels, either affecting the sorption of aromatic compounds onto the scrubber or interacting with the material within the detection cells within the monitors. Measurements of ambient hydrocarbons
25 exclude the possibility that aromatic VOC's cause a significant interference in UV O₃ monitors, but do not preclude the possible influence of oxidized and/or nitrated aromatics. However, as detailed in Sect. 3.2.2, the most plausible explanation for the observed differences between the UV O₃ monitors and the open path spectroscopic instruments was the incorrect calibration factors for the UV monitors.

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(b) A possible interference from ambient particles was not substantiated by diurnal profiles of particle mass below $0.2 \mu\text{m}$ from either previous studies (Moya et al., 2004) or from the MCMA-2003 campaign (Salcedo et al., 2005a, b). Fine particles of diameter $<0.2 \mu\text{m}$ reached a maximum mass concentration in Mexico City during the morning hours, but differences between the UV O_3 monitors and the spectroscopic instruments were largest during the afternoon. PM_{10} measurements at both the CENICA and La Merced sites corroborate this diurnal pattern, also showing maximum particle loadings in the morning (RAMA, 2005). Thus, ambient particles could not have accounted for the observed differences between the UV O_3 monitors and the open path spectroscopic instruments.

3.2.4 UV O_3 monitor on board ARI Mobile Lab

Comparisons of the data from the UV O_3 monitor on board the ARI Mobile Lab with measurements from DOAS, FTIR and other UV O_3 monitors during stationary deployments at all four co-located sites (Table 1b) revealed a degraded performance for this particular monitor. Figure 4 shows the linear regressions for the UV O_3 monitor on the roof of the CENICA headquarters building and the monitor on board the ARI Mobile Lab versus the co-located DOAS-1 open path measurement. The UV O_3 monitor on board the ARI Mobile Lab displayed a negative bias at high ambient O_3 levels and a positive bias at low ambient O_3 levels. This pattern was observed at all four stationary sites in comparisons with both open path and point sampling O_3 measurements indicating that the problem was definitely with the UV O_3 monitor on board the ARI Mobile Lab. This behavior may be partially explained by calibration factor differences but was most likely due to a contaminated particle filter and/or scrubber for this particular monitor. For example, this pattern was consistent with a contaminated particulate filter destroying O_3 at high ambient O_3 levels and releasing particles and/or some UV absorbing species at low ambient O_3 levels. Contamination of this particular particle filter was not surprising given its use on board the ARI Mobile Lab where it directly sampled exhaust plumes from heavy traffic.

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Additionally, a negative interference was observed in the UV O₃ monitor on board the ARI Mobile Lab during routine deliberate zero air purges of the main sampling inlet line, which were for calibration of other instruments sampling from the same inlet as the O₃ monitor. Recent work has shown that this type of behavior is consistent with rapid relative humidity changes influencing the transmission of UV light within the detection cell of the UV O₃ monitor (Wilson, 2005).

In summary, the performance of standard UV O₃ monitors is dependent upon the performance of the particulate filter, which was definitely an issue during this study for the UV O₃ monitor on board the ARI Mobile Lab. Overall, this particular monitor suffered from both the observed aerosol interference (Sect. 3.1) and from a contaminated particulate filter and/or scrubber, such that data from this monitor was excluded from the earlier comparisons.

4 Conclusions

In this study, the performance of several UV O₃ monitors (US EPA Federal Equivalent Method) has been assessed based on data from a recent field campaign in Mexico City. Two of these monitors were co-located with open path DOAS and FTIR measurements of O₃. The O₃ values determined by these UV monitors were systematically different from those determined by the open path instruments, with averaged discrepancies of up to 13%. If uniform span corrections are applied to these two sets of UV O₃ monitor data, the agreement with the co-located open path instruments is within 5% with $R^2 > 0.89$. Comparisons of two co-located open path DOAS O₃ measurements and co-located point sampling and open path CO measurements showed that this level of agreement was adequate for the comparison of a point sampling technique with an open path measurement. Titration of O₃ by NO is shown to influence these comparisons significantly only during morning rush hour when O₃ levels were low and NO_x levels were at their highest. For these two comparisons at the CENICA and La Merced fixed sites, there was no evidence to suggest that the observed differences in measured

O₃ concentration were due to interferences affecting the reported O₃ concentration of the UV O₃ monitors, but such a possibility was not ruled out.

A third UV O₃ monitor employed in this study displayed significant interferences from fresh diesel emissions attributed to fine particles ($D_p < 0.2 \mu\text{m}$) passing through the particulate filter and scattering and/or absorbing radiation within the detection cell. This same monitor also produced biased measurements owing to a contaminated particle filter and/or scrubber.

As discussed in Sect. 3.2.2, the concentration of O₃ was overestimated by the UV O₃ monitor at CENICA and was underestimated by the UV monitor at La Merced. As mentioned, we used the regression slopes for the comparisons of the UV O₃ monitors with the open path spectroscopic instruments to determine a corrected calibration factor for the UV monitors. To assess the larger implications of these incorrect calibration factors, the number of violations of the US EPA's O₃ non-attainment thresholds was determined for the O₃ concentrations as measured by the UV O₃ monitors for 1-h and 8-h standards of 120 ppb and 85 ppb, respectively (Environmental Protection Agency, 2005; Reynolds et al., 2004); see Table 3. (Note that Mexican 1-h and 8-h standards are 110 ppb and 80 ppb, respectively.) Correcting the calibration factor in the UV monitors resulted in a slight decrease in the number of days with violations at CENICA, 10% for 1-h average and 5% for 8-h average, and a relatively large increase in the number of days with violations at La Merced, 61% for 1-h average and 72% for 8-h average. This data was only from the MCMA-2003 campaign and thus represents a limited sample size and limited amount of seasonal variation. However, it is clear that this issue of correct calibration factors can have a major impact on the non-attainment status of a polluted urban area, falsely inflating or deflating the number of violations, potentially by very large amounts.

In summary, we conclude that UV O₃ monitors, if accurately calibrated, have the potential to work well in a heavily polluted urban environment, but that there are significant challenges associated with calibrating and operating these instruments properly. Regardless of new technologies that may become available, use of UV O₃ monitors in

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monitoring networks worldwide will undoubtedly continue for many years to come, and as such, several advances with respect to testing and operation of these instruments should be pursued:

1. Although interferences due to anomalous interactions of relative humidity with the scrubber were not observed in this study, a “wet” calibration procedure that addresses possible interferences owing to varying relative humidity should be developed and new scrubber technology that completely avoids the possibility of these interferences should be pursued (Cavanagh and Verkouteren, 2001).
2. The significant interferences observed from ambient diesel particles mandates that small pore size filters ($0.2\ \mu\text{m}$ or less) that are replaced frequently are necessary for accuracy in urban areas.
3. Previously recommended calibration procedures involving frequent side-by-side comparisons with an O_3 instrument that is maintained in good operating order, preferably employing a different measurement technique (Parrish and Fehsenfeld, 2000), should be adopted by routine users of UV O_3 monitors in addition to whatever calibration practices are currently employed.
4. Although this study was able to reach conclusions employing comparisons of the integrated O_3 concentration over a long light path with a point sampling measurement, spatial and temporal inhomogeneities necessarily limit the ultimate precision of such comparisons. Future studies could avoid this limitation by comparing UV O_3 monitors side-by-side with point sampling spectroscopic instruments. Potential spectroscopic point sampling techniques include tunable infrared laser differential absorption spectroscopy (TILDAS), folded light path FTIR and folded light path UV-DOAS. We encourage future field studies that incorporate point sampling spectroscopic O_3 measurement techniques to operate co-located with a standard UV O_3 monitor so as to more definitively evaluate the performance of this standard measurement technique.

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Table 1. Regression coefficients and corresponding R^2 values for linear least square best-fits for standard UV O_3 monitor measured concentrations versus open path DOAS and FTIR measurements at CENICA and La Merced sites. Similar comparisons for CO instruments are included for reference (see Sect. 3.2.1).

(a) UV O_3 monitor comparison with open path measurements	Regression slope	Regression intercept (ppb for O_3 and ppm for CO)	Correlation coefficient R^2
CENICA UV vs MIT DOAS-1	1.08	1.1	0.97
CENICA UV vs MIT DOAS-2	1.08	0 (forced)	0.97
CENICA UV vs MIT DOAS-2	1.13	-4.6	0.95
La Merced RAMA UV vs UNAM DOAS	0.82	-3.7	0.89
La Merced RAMA UV vs UNAM FTIR	0.90	-4.4	0.96
(b) Open path DOAS comparison			
CENICA DOAS-2 vs DOAS-1	0.93	5.9	0.96
CENICA DOAS-2 vs DOAS-1	1.01	0 (forced)	0.96
(c) CO monitor comparison with open path measurements			
CENICA Monitor vs CTH FTIR	0.96	0.1	0.93
La Merced RAMA Monitor vs UNAM FTIR	0.97	0 (forced)	0.70
La Merced RAMA Monitor vs UNAM FTIR	0.67	0.94	0.70
(d) ARI Mobile Lab UV O_3 monitor comparisons			
ARI Mobile Lab UV vs MIT DOAS-1 at CENICA	0.56	6.0	0.88
ARI Mobile Lab UV vs UNAM FTIR at La Merced	0.47	11.6	0.90
ARI Mobile Lab UV vs RAMA UV at Pedregal	0.60	9.0	0.90
ARI Mobile Lab UV vs CENICA UV at Santa Ana	0.75	0.0	0.95

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Table 2. Regression coefficients and corresponding R^2 values for linear least square best-fits for corrected standard UV O_3 monitor measured concentrations versus open path DOAS and FTIR measurements at CENICA and La Merced sites. Correction factors determined from regressions slopes listed in Table 1.

UV O_3 monitor comparison with open path measurements	Correction factor applied to UV O_3 monitor	Regression slope	Correlation coefficient R^2
CENICA UV vs MIT DOAS-1	1.1	0.94	0.90
CENICA UV vs MIT DOAS-2	1.18	0.96	0.89
La Merced RAMA UV vs UNAM DOAS	0.92	0.99	0.97
La Merced RAMA UV vs UNAM FTIR	0.92	1.04	0.95

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Table 3. Number of hour-long averaged O₃ concentrations that exceeded the EPA's one-hour average threshold of 120 ppb, number of days that included at least one hour-long averaged O₃ concentration above this threshold, and number of days that included an eight-hour long averaged O₃ concentration above the EPA's eight-hour average threshold of 85 ppb. Data are for the different O₃ instruments at the CENICA and La Merced sites and are for the days during the MCMA-2003 campaign where the instruments were operating properly (27 days at CENICA and 34 days at La Merced).

Instrument	Number of hours with 1 h average violations	Number of days with 1 h average violations	Number of days with 8 h average violations
CENICA			
UV O ₃ Monitor	55	19	20
UV O ₃ Monitor Corrected	37	17	19
La Merced			
UV O ₃ Monitor	21	13	11
UV O ₃ Monitor Corrected	50	21	19

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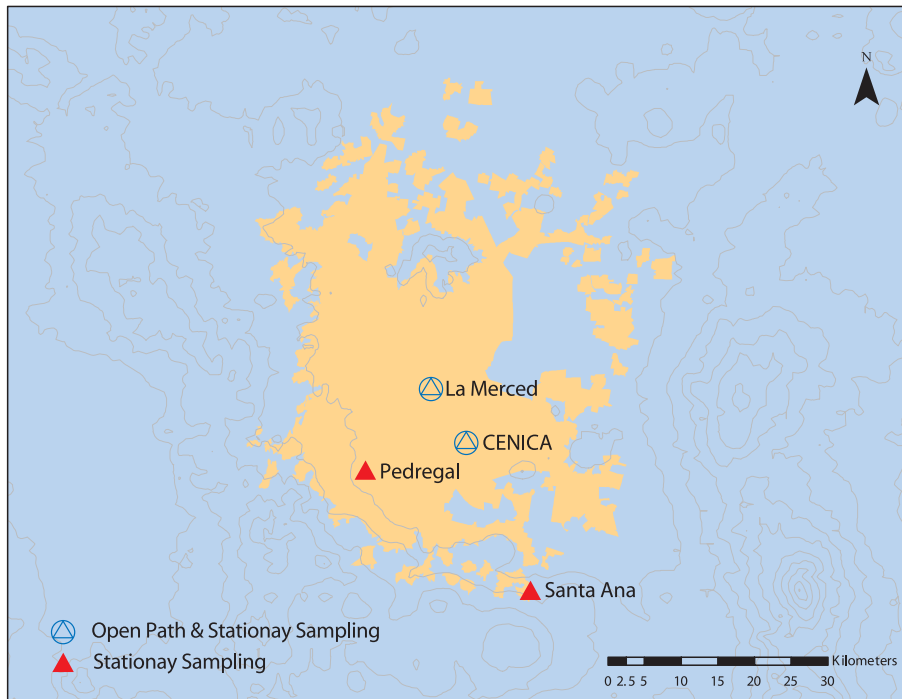


Fig. 1. Map of the Metropolitan Mexico City Area (MCMA). The figure shows the urbanized sections of the city in shaded orange, along with the key topographic contours (grey). The names and locations of the fixed sites described in this work are marked on the map. The open triangles represent points where either the CENICA open path systems or the UNAM open path were located. The filled triangles describe the sites where the Mobile Laboratory was co-located with the stationary sampling O₃ monitors. See text (Sect. 2) for a description of the neighborhood and character of each site.

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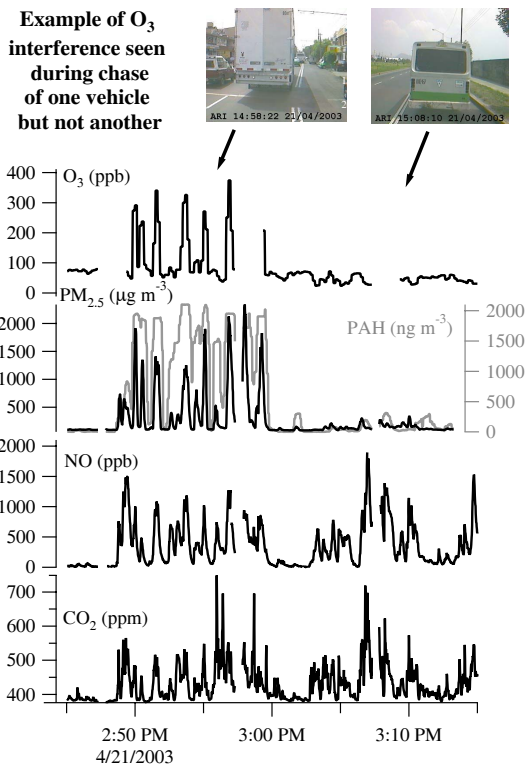


Fig. 2. Time series showing an interference problem for the O₃ instrument while chasing two separate vehicles. In the first chase of a diesel truck, apparent O₃ levels reached up to 400 ppb during obvious combustion plumes; in the second chase of a non-diesel microbus, there was no interference. The NO signal was derived from a total NO_y measurement minus measured NO₂; it was assumed that all NO_y in a fresh combustion plume was either NO or NO₂. The O₃ interference correlated best with the PM_{2.5} and PAH measurements. The gaps in the time traces are from deliberate zero air purges of the inlet line. Instrument lag times have been adjusted for such that displayed time traces represent the time at the inlet tip. Instrument response times have not been adjusted.

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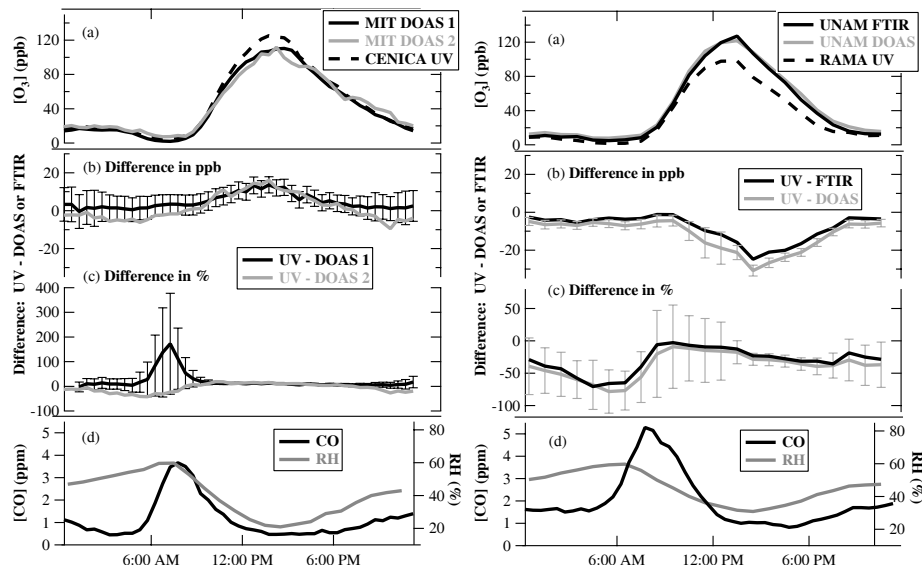


Fig. 3. Diurnally averaged profiles of O_3 concentrations for the entire MCMA-2003 field campaign as measured at the CENICA (left panel) and La Merced (right panel) sites are displayed in panel (a). The diurnally averaged profile of the difference between the UV O_3 monitor and the corresponding long path spectroscopic measurement are shown on an absolute scale (b) and as a percentage of the measured O_3 concentration (c). Note: these are not the differences of the diurnal profiles, they are the diurnal profiles of the differences. The diurnally averaged profiles of the measured CO concentrations and ambient relative humidity at both locations are also shown for reference (d). For the CENICA site, the CO concentration as measured by the CENICA rooftop monitor is shown; for the La Merced site, the CO concentration from the UNAM FTIR instrument is shown. For clarity, 1σ uncertainty error bars are placed on only one of traces for differences between UV O_3 monitor and corresponding open path spectroscopic measurement (at CENICA uncertainties are displayed for the CENICA UV monitor – DOAS 1; at La Merced for the RAMA UV monitor – UNAM DOAS); the uncertainties for the other difference traces were comparable to those shown.

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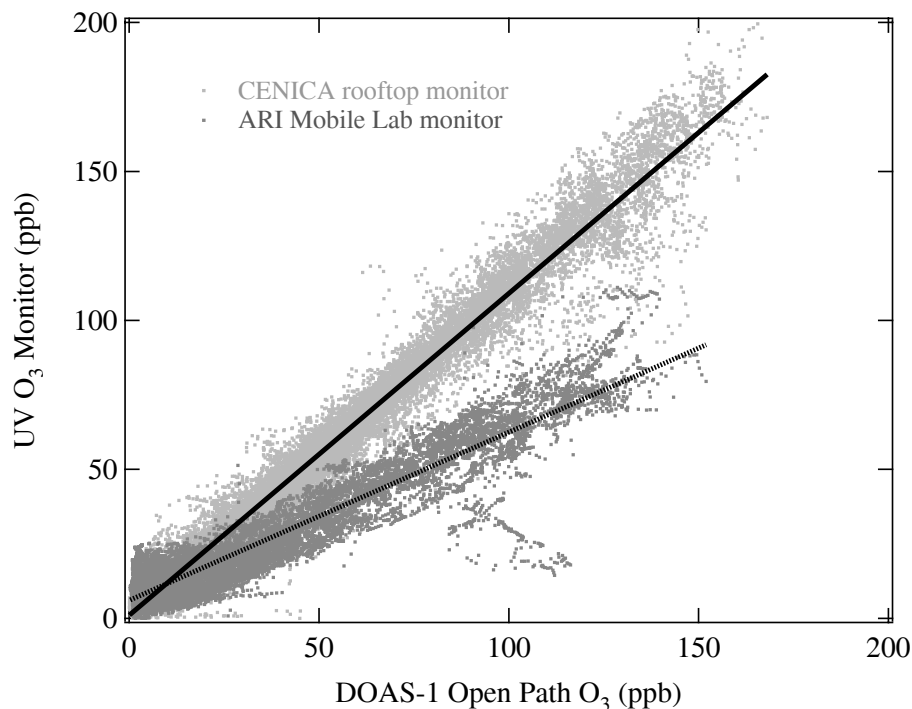


Fig. 4. Linear regressions for UV O₃ monitors versus DOAS-1 open path measurement of O₃ at CENICA site. Data from two different UV O₃ monitors is shown: the CENICA monitor located on the roof of their headquarters building (light gray points) and the monitor on board the ARI Mobile Lab (dark gray points). The linear fits (with 2 σ uncertainties reported from the fit only) are:

CENICA rooftop monitor (solid line): slope=1.08 \pm 0.01, intercept=1.1 \pm 0.1, R²=0.97

ARI Mobile Lab monitor (dashed line): slope=0.56 \pm 0.01, intercept=6.0 \pm 0.1, R²=0.88.

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