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Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment

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Abstract

Data from a recent field campaign in Mexico City are used to evaluate the performance of the EPA Federal Reference Method for monitoring ambient concentrations of NO_2. Measurements of NO_2 from standard chemiluminescence monitors equipped with molybdenum oxide converters are compared with those from Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) and Differential Optical Absorption Spectroscopy (DOAS) instruments. A significant interference in the chemiluminescence measurement is shown to account for up to 50% of ambient NO_2 concentration during afternoon hours. As expected, this interference correlates well with non-NO_x reactive nitrogen species (NO_z) as well as with ambient O_3 concentrations, indicating a photochemical source for the interfering species. A combination of ambient gas phase nitric acid and alkyl and multifunctional alkyl nitrates is deduced to be the primary cause of the interference. Observations at four locations at varying proximities to emission sources indicate that the percentage contribution of HNO_3 to the interference decreases with time as the air parcel ages. Alkyl and multifunctional alkyl nitrate concentrations are calculated to be reach concentrations as high as several ppb inside the city, on par with the highest values previously observed in other urban locations. Averaged over the MCMA-2003 field campaign, the CL NO_x monitor interference resulted in an average measured NO_2 concentration up to 22% greater than that from co-located spectroscopic measurements. Thus, this interference has the potential to initiate regulatory action in areas that are close to non-attainment and may mislead atmospheric photochemical models used to assess control strategies for photochemical oxidants.

1 Introduction

Nitrogen oxides NO_x= sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2) are primarily emitted as byproducts of combustion and participate in ozone (O_3) formation and destruction, thus playing a key role in determining the air quality in urban environ-

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ments (Finlayson-Pitts and Pitts, 2000). NO_2 is designated as one of the United States Environmental Protection Agency's (US EPA) "criteria pollutants", which also include O_3, carbon monoxide (CO), sulfur dioxide (SO_2), airborne lead (Pb) and particulate matter (PM). The US EPA initiates regulatory action if an urban area has criteria pollutant concentrations that exceed a certain threshold (either one hour averaged daily maxima, eight hour averaged daily maxima or annually averaged concentrations), referred to as being in "non-attainment." While no counties in the US are currently in non-attainment for NO_2, the US EPA has recently announced sweeping new regulations aimed at reducing NO_x levels by 2015 (Environmental Protection Agency, 2005). Therefore, accurately measuring the concentration of NO_2, as mandated under the 1990 Clean Air Act Amendments, Section 182 (c)(1) (Demerjian, 2000), will become increasingly important. Positive interferences in the measurement of NO_2 may lead to the false classification of an urban area as being in non-attainment.

In addition to the regulatory purposes of monitoring, ambient measurements are also used by air quality models (AQM) for characterization and prediction of future high ozone episodes (Demerjian, 2000). Adequate diagnostic testing of AQM's requires uncertainties in NO_2 measurements of less than ±10% (Environmental Protection Agency, 2001; McClenny et al., 2002). There has also been considerable attention paid recently to the direct emissions of NO_2 from diesel vehicles (Friedeburg et al.,2005; Jenkin, 2004a; Jimenez et al., 2000; Latham et al., 2001; Pundt et al., 2005) and their resulting health effects (Beauchamp et al., 2004). These and other studies that rely on the data from monitoring networks, such as recent NO_2 source apportionment (Carslaw and Beevers, 2004; 2005) and oxidant partitioning (Jenkin, 2004b) studies, could be significantly affected by interferences in the standard methods for NO_2 measurement. In summary, assuring that NO_2 monitors routinely achieve a high level of precision is important for the accurate prediction of air quality.

Of the various techniques for measuring *in situ* NO and NO_2 concentrations, the most prevalent, and the Federal Reference Method as designated by the US EPA, is the chemiluminescence instrument (CL NO_x monitors) (Demerjian, 2000). This tech-

nique has been described in detail elsewhere (Fontjin et al., 1970; Ridley and Howlett, 1974). Briefly, it is based on the chemiluminescent reaction of NO with O_3 to form electronically excited NO_2, which fluoresces at visible and near infrared wavelengths. The technique is simple and relatively reliable. The detection sensitivity benefits from small background signal levels because no light source is necessary to initiate the fluorescence. Only an O_3-generating lamp and a modestly cooled photomultiplier (typically $\sim -4^{\circ}C$) are required; thus CL NO_x monitors are relatively inexpensive. Calibration involves the sampling of a known standard to determine the absolute response of the instrument; such standards are readily acquired. CL NO_x monitors typically operate in a mode that alternates between two states: one that measures the concentration of NO by sampling ambient air directly, and one that measures the sum of NO and NO_2 by passing the ambient air stream over a catalyst (usually gold or molybdenum oxide, often heated) to convert NO_2 to NO. The difference of the two values is reported as the NO_2 concentration. Although instruments are available that utilize a flash lamp or laser to convert NO_2 to NO, this study only examines CL NO_x monitors with molybdenum oxide catalysts, which are the most prevalent type (Parrish and Fehsenfeld, 2000).

In addition to the advantages of CL NO_x monitors listed above, however, there are known interferences for this standard technique; see several recent reviews (Cavanagh and Verkouteren, 2001; Demerjian, 2000; Environmental Protection Agency, 1993; McClenny et al., 2002; Parrish and Fehsenfeld, 2000; Sickles, 1992). The most significant issue with standard CL NO_x monitors is their inability to directly and specifically detect NO_2. It has been well established that other gas phase nitrogen containing compounds are converted by molybdenum oxide catalysts to NO and therefore can be reported as NO_2 by a standard CL NO_x monitor (Winer et al., 1974). As stated by the US EPA, "chemiluminescence $NO/NO_x/NO_2$ analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. Atmospheric concentrations of these potential interferences are generally low relative to NO_2 and valid NO_2 measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known

or suspected to be high relative to NO_2, the use of an equivalent method for the measurement of NO_2 is recommended." (Environmental Protection Agency, 2006) Additionally, manufacturers now use this same technology to make total reactive nitrogen (NO_y) measurements. Molybdenum oxide catalysts are known to efficiently reduce compounds such as NO_2, NO_3, HNO_3, N_2O_5, CH_3ONO_2, $CH_3CH_2ONO_2$, n-$C_3H_7ONO_2$, n-$C_4H_9ONO_2$, and CH_3CHONO and to a lesser extent also reduce HO_2NO_2, HONO, RO_2NO_2, NH_3 and particulate phase nitrate. These catalysts do not efficiently reduce N_2O, HCN, CH_3CN or CH_3NO_2 at typical operating converter temperatures lower than 400˚C (Fehsenfeld et al., 1987; Williams et al., 1998). To emphasize this point, consider that the only difference between CL NO_x and NO_y monitors is the position of the catalyst: in a CL NO_y monitor, the catalyst is placed very close to the front of sampling inlet so as to convert all NO_y species, whereas in a CL NO_x monitor, the catalyst is placed after a particulate filter and just before the detection chamber, allowing the conversion and detection as "NO_2" of any gas phase nitrogen containing compounds not removed by passive loss on surfaces upstream of the converter.

Other more specific NO_2 detection techniques have been developed, including a photolysis technique to specifically convert NO_2 to NO that avoids using a metal catalyst while still employing the chemiluminescence reaction (Kley and McFarland, 1980), an LIF technique (Thornton et al., 2000; Thornton et al., 2003), a fast gas chromatography luminol chemiluminescence detection (Marley et al., 2004), Differential Optical Absorption Spectroscopy (DOAS)(Platt, 1994; Platt and Perner, 1980), and a Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) technique (Li et al., 2004) (also described below). Several recent reviews provide a more complete description of these and other NO_2 measurement techniques (Demerjian, 2000; McClenny et al., 2002; Parrish and Fehsenfeld, 2000). Although several of these instruments have been shown to perform well in intercomparisons (Fehsenfeld et al., 1990; Gregory et al., 1990), the majority of these techniques are, at this time, research grade instruments unsuitable for use in routine monitoring. A newer technique, Cavity Attenuated Phase Shift (CAPS) spectroscopy, has shown the potential to provide accurate spectroscopic

measurements of NO_2 (0.3 ppb detection limit in <10 s) at a reasonable cost (Kebabian et al., 2005), but it is still in the development phase. Even if these other techniques gain prevalence in the coming years, the current widespread use of CL NO_x monitors makes understanding and quantifying interferences to this technique critical. Recent field studies have begun to quantify the magnitude of interferences to this technique, for example (Li et al., 2004) have shown a consistent positive measurement bias from CL NO_x monitors relative to an absolute TILDAS measurement of NO_2. However, to our knowledge no field intercomparisons have sought to directly quantify this interference and characterize the specific compounds responsible for it.

This study uses data from the recent Mexico City Metropolitan Area (MCMA) field campaign during spring of 2003 (MCMA-2003), which featured a comprehensive suite of both gas and particle phase instrumentation from numerous international laboratories, including multiple measurements of NO_2 (de Foy et al., 2005; Molina and Molina, 2006). Here, we utilize this unique data set to evaluate the performance of standard CL NO_x monitors in a heavily polluted urban atmosphere, examine possible interferences and make recommendations for monitoring networks in general. Data from an exploratory field mission in the MCMA during February of 2002 are also presented.

2 Measurements

A major part of the MCMA-2002 and 2003 campaigns was the deployment of the Aerodyne Research, Inc. Mobile Laboratory (ARI Mobile Lab), a van equipped with a comprehensive suite of research grade gas and particle phase instrumentation (Herndon et al., 2005; Kolb et al., 2004). The ARI Mobile Lab had two modes of operation during the campaigns: mobile and stationary. In mobile mode, the main objectives were either sampling of on-road vehicle exhaust or mapping of emission sources. In stationary mode, the ARI Mobile Lab was parked at a chosen site, typically making measurements for several days in a row. Stationary mode data in this study will be presented from four sites from the 2002 and 2003 field campaigns, which are described in detail elsewhere

(Dunlea et al., 2006); briefly they are (1) CENICA (Centro Nacional de Investigacion y Capacitacion Ambiental) – the "supersite" for the MCMA-2003 campaign located on a university campus to the south of the city center, which receives a mix of fresh pollution from area traffic corridors and aged pollution from more downtown locations, (2) La Merced – a downtown location near an open market and a large traffic corridor, (3) Pedregal – an affluent residential neighborhood downwind of the city center, and (4) Santa Ana – a boundary site outside of the city, which receives mostly aged urban air during the day and rural air overnight.

The instruments on board the ARI Mobile Lab most relevant to this study were a TILDAS NO_2 instrument and a standard CL NO_x monitor. The TILDAS technique for measuring NO_2 has been described in detail elsewhere (Li et al., 2004) and only a brief description is presented here. TILDAS is a tunable infrared laser differential absorption measurement that employs a low volume, long path length astigmatic Herriott multipass absorption cell (McManus et al., 1995) with liquid nitrogen cooled laser infrared diodes and detectors. The laser line width is small compared to the width of the absorption feature and the laser frequency position is rapidly swept over an entire absorption feature of the molecule to be detected, NO_2 in this case. Accurate line strengths, positions and broadening coefficients are taken from the HITRAN data base (Rothman et al., 2003). Reference cells containing the gas of interest are used to lock the laser frequency position. Of the species in the HITRAN database in the $NO_2\nu_2$ wavelength region (1600 cm^{-1}), the next strongest absorber (CH_4) has nearby absorption lines which are six orders of magnitude weaker than the NO_2 lines used in these measurements. Additionally, the CH_4 lines are frequency shifted away from the main NO_2 features and this is resolved with the typical linewidth of the lead salt diode lasers used. Therefore, the measurements of NO_2 by tunable diode laser spectroscopy are believed to be interference-free. The mode purity of the diode was verified by measuring 'black' NO_2 lines in a reference cell along another optical path present in the instrument. The absolute accuracy of the concentrations measured by TILDAS is largely determined by how well the line strengths are known. For the absorption lines used

in the two instrument channels, measuring NO and NO_2 respectively, the presently accepted band strengths are known to within 6% for NO and 4% for NO_2 (Smith et al., 1985). It is important to note that this technique is an absolute concentration measurement, which does not require a calibration, and thus served as the benchmark against which to compare other NO_2 measurements.

Standard CL NO_x monitors have been described above and here we briefly describe the calibrations performed during the MCMA-2003 campaign. The standard calibration procedure involves zeroing the monitors while measuring NO_x-free air and then adding several specified amounts of NO to the instrument covering the desired operating range. The CL NO_x monitor on board the ARI Mobile lab was calibrated six times during the campaign, utilizing several different standardized mixtures of NO in nitrogen and NO/CO/SO_2 in nitrogen and resulting in no greater than an 8% deviation. Early in the campaign, technicians from RAMA, Red Automática de Monitoreo Ambiental (RAMA, 2005), calibrated both the CL NO_x monitor on board the Mobile Lab and the one on the CENICA rooftop during the same afternoon for consistency. RAMA operates 32 monitoring sites around the MCMA, many of which are equipped with standard CL NO_x monitors, all of which are calibrated via this same method. The RAMA network has been audited by the US EPA (Environmental Protection Agency, 2003), and was concluded to be "accurate and well-implemented".

For this study, measurements from the ARI Mobile Lab are used in conjunction with measurements from instruments at the various stationary sites. The instrumentation at the CENICA site included two long-path DOAS (LP-DOAS) instruments (Platt, 1994; Platt and Perner, 1980; Volkamer et al., 1998) which measured NO_2 amongst a suite of other compounds. The detection limits for NO_2 were 0.80 and 0.45 ppb for DOAS-1 and DOAS-2 respectively (see companion paper (Dunlea et al., 2006) for more detail on CENICA site). The La Merced site also included side-by-side open path Fourier transform infrared (FTIR) and DOAS instruments (Grutter, 2003). Both instruments measured numerous gas-phase compounds, but only data from the FTIR measurement of nitric acid (HNO_3; detection limit of 4 ppb) and from the DOAS measurement

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of NO_2 (detection limit of 3 ppb) are shown here.

3 Results and Discussions

3.1 Observation of Interference

Simultaneous measurements of NO_2 on board the ARI Mobile Lab by the CL NO_x monitor and the TILDAS instrument revealed a recurring discrepancy where the CL NO_x monitor reported a higher NO_2 concentration than the TILDAS instrument. We consider the TILDAS measurement to be an absolute concentration measurement and thus this discrepancy is concluded to be an interference in the CL monitor. We define this "CL NO_x monitor interference" as the CL NO_x monitor NO_2 measurement minus a co-located spectroscopic NO_2 measurement.

$$\mathrm{CLNO_x monitor\ \ interference} = [\mathrm{NO_2}](\text{CL monitor}) - [\mathrm{NO_2}]\,(\text{spectroscopic}) \quad (1)$$

Figure 1 shows the CL NO_x monitor interference as observed during both the 2002 and 2003 field campaigns. The CL NO_x monitor interference was observed to occur daily, peaking in the afternoons during periods when ambient O_3 levels were highest. The CL NO_x monitor interference accounted for as much as 50% of the total NO_2 concentration reported by the CL NO_x monitor (30 ppb out of a reported 60 ppb for the 2002 campaign and 50 ppb out of 100 ppb for the 2003 campaign). The interference was observed at all fixed site locations visited by the ARI Mobile Lab, but was more readily detectable at the urban sites than the Santa Ana boundary site, owing simply to the lower overall NO_2 levels at the boundary site. Additionally, this CL NO_x monitor interference was present when comparing DOAS long path measurements of NO_2 to CL NO_x monitors at both the CENICA and La Merced sites. For these sites, the CL NO_x monitor interference was more variable in time owing to the loss of spatial coherence when comparing a long path measurement with a point sampling data for a reactive species for further

discussion of open path versus point sampling comparison, see Dunlea et al. (2006) and San Martini et al.(2006a).

The observation of such large CL NO_x monitor interference levels directly contradicts previous conclusions that this will only be an issue at rural or remote locations (Jenkin, 2004b). In summary, the CL NO_x monitor interference was observed to occur regularly and to roughly correlate with the ambient O_3 concentration; the subsequent section will explore the cause of this interference in more detail.

3.2 Examination of Possible Sources of Interference

Three potential sources for the interference in the chemiluminescence NO_2 measurement using the available supplementary data from the MCMA 2003 campaign are explored: (1) gas phase olefinic hydrocarbons, (2) gas phase ammonia and (3) some portion of the non-NO_x fraction of reactive nitrogen (NO_z).

3.2.1 Gas Phase Olefins

The chemiluminescent reaction of ambient gas phase olefins with excess O_3 within the CL NO_x monitor reaction chamber, where the resulting fluorescence is recorded as NO_2, is a potential interference to the CL NO_x monitor. However, no correlation of the measured CL NO_x monitor interference was observed with olefin concentrations measured during the MCMA-2003 field campaign. Olefin measurements were made using a Proton Transfer Reaction Mass Spectrometer (PTRMS) on board the ARI Mobile Lab and a Fast Isoprene Sensor (FIS) at the CENICA supersite. In the PTRMS, mass to charge ratios of m/z43 and 71 are representative of the ambient olefin levels; the signals at these masses are primarily comprised of propylene and pentene compounds respectively (Rogers et al., 2006). The FIS employs the chemiluminescent reaction of olefinic compounds with O_3 (Velasco et al., 2006). Both the PTRMS and the FIS measured olefin levels were high enough to potentially account for the CL NO_x monitor interference, however, neither measurement correlated in time with the interference.

Results from the linear correlation plots are listed in Table 1. The daily peak in the olefin levels was observed during the morning hours, which does not coincide with the afternoon peak in the CL NO_x monitor interference. Based on these observations, we conclude that gas phase olefins did not contribute significantly to the observed CL NO_x monitor interference.

3.2.2 Gas Phase Ammonia

A second possibility for the cause of the CL NO_x monitor interference is gas phase ammonia (NH_3), which has been shown to be converted by molybdenum oxide catalysts with an efficiency somewhere between a few percent (Williams et al., 1998) and 10% (Shivers, 2004). A TILDAS system utilizing a Quantum Cascade Laser (QCL) to monitor gaseous ammonia was deployed on board the ARI Mobile Lab for the MCMA-2003 campaign allowing direct *in situ* side-by-side measurements of NH_3 and the CL NO_x monitor interference. Measured ambient NH_3 concentrations were typically less than 30 ppb (and only very rarely exceeded 100 ppb), translating to potential interferences in the chemiluminescence NO_2 measurement on the order of less than 3 ppb, not enough to account for the regularly observed interferences around 10–20 ppb. Additionally, NH_3 concentrations peaked during the morning before the break up of the boundary layer (earlier than 11 AM local time), indicating a significant source from automobiles (San Martini et al., 2006a), which does not correspond to the afternoon maxima in the CL NO_x monitor interference. For all sites visited by the ARI Mobile Lab, the slopes of the linear least-squares fit correlation plots of the CL NO_x monitor interference versus the measured NH_3 concentrations were less than 0.34 and R^2 values did not exceed 0.17, indicating no significant correlation (see Table 1). We conclude that gas phase NH_3 did not contribute significantly to the observed CL NO_x monitor interference.

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3.2.3 The Non-NO_x Fraction of Reactive Nitrogen (NO_z)

It has been long established that molybdenum converters within standard CL NO_x monitors have a potential interference in the NO_2 measurement due to gas phase reactive nitrogen compounds (Demerjian, 2000; Environmental Protection Agency, 2006; Parrish and Fehsenfeld, 2000). The ARI Mobile Lab as configured for the MCMA-2003 campaign included a total NO_y instrument (TECO 49C), which measures both NO_y and NO using the chemiluminescence technique, but configured differently than a standard CL NO_x monitor so as to purposely exploit the molybdenum converter's ability to detect more gas phase reactive nitrogen species. From the CL NO_y monitor NO_y and NO measurements, along with the TILDAS NO_2 measurement, we calculated the non-NO_x fraction of NO_y, referred to as NO_z. Table1 lists the results of linear least-squares fits of the correlation plots of the CL NO_x monitor interference versus NO_z at the various locations visited by the ARI Mobile Lab. The CL NO_x monitor interference level varied linearly with the NO_z concentration, and was smaller in magnitude, indicating that some portion of NO_z was responsible for the interference. Fair to good correlation (R^2 = 0.32–0.79) was observed at all sites visited by the ARI Mobile Lab, with ratios of the CL NO_x monitor interference to NO_z = (0.44–0.66). Thus, the obvious and expected conclusion is that some reactive nitrogen compound or compounds are the cause of the observed CL NO_x monitor interference.

This type of comparison has a number of inherent limitations. Negative values for the CL NO_x monitor interference are often recorded because this calculated value is the subtraction of two measurements. In general, more variance in this subtracted quantity is expected when an open path spectroscopic measurement is subtracted from a point sampling CL NO_x monitor measurement, limiting the achievable R^2 values for these correlation plots. We also note here that the onset of the daily rise of the CL NO_x monitor at CENICA is delayed relative to the other three sites by ~2 h: from 10 AM onset elsewhere to 12 PM onset at CENICA. CENICA also experiences the highest percentage of negative CL NO_x monitor interference measurements indicating that the open

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path DOAS light paths may be influenced by NO_x sources, such as roadways underneath the light paths, which do not advect to the CENICA rooftop sampling location. (San Martini et al., 2006b) have discussed the limitations of this NO_z measurement in more detail.

As shown in Figs. 1 and 3, the CL NO_x monitor interference peaked in magnitude during the afternoons, corresponding to peaks in the ambient O_3 concentration. Plotting the CL NO_x monitor interference versus the co-located measured O_3 concentration shows fair correlation at all locations (R^2=0.19–0.54); see Fig. 2 and Table 1. The measured slopes of these correlation plots indicate that the magnitude of the CL NO_x monitor interference concentration was (6–19)% of the ambient O_3 concentration, with an average of 10%. O_3 levels within the detection chamber of these CL NO_x monitors are three orders of magnitude higher than ambient levels (Shivers, 2004); thus ambient O_3 levels will not significantly influence the detection of NO in the CL NO_x monitors. The difference in residence time in the sampling lines to the CL NO_x monitor compared to the TILDAS instrument was small enough (<3 s) to preclude the reaction of ambient NO with ambient O_3 from contributing significantly to the measured differences in NO_2 concentrations. Additionally, the measured CL NO_x monitor interference showed a poor correlation with the product of ambient concentrations of [NO]*[O_3] (regression R_2=0.03). Lastly, the reaction of NO_2 with ambient O_3 in the sampling inlet would not contribute to the observed interference, as this reaction only serves to convert NO_2 to NO_3, which would readily be converted to NO on the molybdenum catalyst and then recorded as NO_2. Thus, our conclusion is that the CL NO_x monitor interference was not due to O_3 itself, but was primarily due to reactive nitrogen species that are produced photochemically along with O_3.

We now examine the individual species that make up NO_z in order to determine the most likely contributors to the CL NO_x monitor interference. We start by removing from consideration those reactive nitrogen species which are not converted by the molybdenum oxide catalyst, e.g., amines (Winer et al., 1974), or whose concentrations do not peak during the afternoon, specifically nitrous acid (HONO), other organic nitrites,

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the nitrate radical (NO_3) and N_2O_5. HONO was measured directly by the DOAS instrument at the CENICA supersite and observed to have its highest concentrations during the morning. Other organic nitrites are unlikely to have concentrations that approach ppb levels and will have photolytic loss rates that maximize in the afternoon, making it very unlikely that they could contribute significantly to the observed CL NO_x monitor interferences. Lastly, measured concentrations of NO_3 and N_2O_5 are observed almost exclusively at night, excluding them from possible contribution to the observed daytime interference. Thus, our most likely candidates are (a) particulate nitrate, (b) peroxyacetyl nitrate and other peroxyacyl nitrates, (c) nitric acid (d) alkyl and multifunctional alkyl nitrates and (e) a combination of more than one of these species.

(a) Particulate phase nitrate (pNO_3^-) may be converted by the CL NO_x monitor and reported as NO_2 if sufficiently small particles can penetrate the particulate filter on the CL NO_x monitor. The particulate filter on a CL NO_x monitor typically filters out particles with diameters larger than 200 nm. In the MCMA-2003 campaign, Aerodyne Aerosol Mass Spectrometers (AMSs)(Jayne et al., 2000) on board the ARI Mobile lab and on the roof of the CENICA building measured the size-resolved chemical composition of the non-refractory component of ambient particles smaller than 1.0 μm, including pNO_3^-. The AMS measurements from MCMA-2003 reveal that only a small fraction of the particle mass was found to be contained in particles with diameters <200 nm, (see Salcedo et al., 2006 for a description of the general aerosol characteristics in Mexico City as observed in MCMA-2003 and previous aerosol studies). Thus, of the measured levels of submicron pNO_3^-, only a small fraction would be expected to enter a CL NO_x monitor resulting in a potential interference.

Diurnal profiles of pNO_3^- (Fig. 3) show that concentrations of submicron pNO_3^- (as converted to its equivalent gas phase concentration) observed in Mexico City were significantly smaller than the CL NO_x monitor interference. At all sites and times, a minimum of 150% of the measured submicron pNO_3^- would be required to explain all of the NO_2 interference. Particulate nitrate from particles with diameters <200 nm is therefore negligible compared to the CL NO_x monitor interference. Additionally, the

diurnal profiles in Fig. 3 show that the maximum in pNO_3 occurs in the morning, a few hours before the maximum in the CL NO_x monitor interference. Table 1 reports only a weak correlation (R^2<0.15) of the CL NO_x monitor interference with the measured ambient submicron pNO_3^- levels for all sites. Overall, it is clear that pNO_3^- does not contribute significantly to the observed CL NO_x monitor interference in Mexico City.

(b) Peroxyacetyl nitrate (PAN) is often found in large quantities in urban atmospheres and concentrations >30 ppb have been observed in the past in Mexico City (Gaffney et al., 1999) The MCMA-2003 field campaign included a PAN measurement at the CENICA supersite (Marley et al., 2004). The diurnal profile of PAN during the MCMA-2003 campaign (Fig. 3b) shows a peak in mid-morning (~10 AM), with concentrations tapering off during the afternoon; this does not match the diurnal pattern of the CL NO_x monitor interference. Additionally, the measured PAN concentrations in MCMA-2003 were significantly lower than previously measured, with maximum PAN levels <15 ppb. The results of the correlation plots of the CL NO_x monitor interference versus the measured PAN concentrations on the CENICA rooftop show an R^2=0.09. PAN and similar peroxyacyl nitrate compounds are therefore concluded to not contribute significantly to the observed CL NO_x monitor interference in Mexico City.

Modeling studies of the outflow of pollution from Mexico City (Madronich, 2006) and more recent measurements downwind of the city (Farmer et al., 2006) show that peroxyacyl nitrate compounds can account for a significant fraction of the NO_z budget in the outflow from Mexico City. Thus, PAN may contribute more significantly to this interference in other locations that experience higher PAN concentrations, but not for the locations within Mexico City that were part of this study.

(c) Nitric acid (HNO_3) is photochemically produced within urban atmospheres and has been observed in significant concentrations in Mexico City (Moya et al., 2004). Production of HNO_3 is generally on the same time scale as production of O_3, since both involve the formation of NO_2. O_3 is formed when NO_2 photolyzes via a two step process:

$$NO_2 + h\nu \rightarrow NO + O \quad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (3)$$

(where M represents a third body colliding molecule, presumably N_2 or O_2). HNO_3 is formed from the association reaction of OH with NO_2

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad (4)$$

The formation of HNO_3 is thus dependent on the competition between reactions (2) and (4). The measured concentrations of NO_2 and OH during MCMA-2003 (Volkamer et al., 2005) indicate that HNO_3 production rates via reaction (4) are quite large (>15 ppb hr^{-1} at maximum). However, losses for HNO_3 within an urban area are also significant, and the ambient concentration depends on the balance between the production and loss rates. In the presence of NH_3, HNO_3 will readily form particle phase ammonium nitrate (NH_4NO_3). HNO_3 is also readily lost on surfaces by dry deposition (Neuman et al., 1999), but there is a large range of deposition velocities in the literature (4–26 cm s^{-1}) and an exact loss rate is difficult to estimate (Neuman et al., 2004; Wesely and Hicks, 2000). It is thus preferable to rely on measurements of HNO_3 as much as possible. During the MCMA-2003 campaign, the only direct HNO_3 concentration measurements were from the open path FTIR operated by the UNAM group at the La Merced site (Flores et al., 2004; Moya et al., 2004). Although the measured HNO_3 concentrations show reasonably good correlation with the CL NO_x monitor interference concentrations (R^2=0.44), the slope of the correlation plot (1.41) indicates that HNO_3 accounts for ~60% of the CL NO_x monitor interference.

For the locations that did not have a measurement of HNO_3, we use modeled values to estimate the possible contribution of HNO_3 to the CL NO_x monitor. San Martini et al. (San Martini et al., 2006a; 2006b) have used an ISORROPIA model embedded in a Markov Chain Monte Carlo algorithm to analyze aerosol data and to predict the gas phase HNO_3 concentrations at the locations included in this study. Diurnal profiles of these predicted HNO_3 concentrations are included in Fig. 3. In general, HNO_3 levels are shown to be large enough to account for the measured CL NO_x monitor interference. However, we note that the measured HNO_3 concentrations at La Merced are

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lower than the predicted levels. We therefore generally conclude that HNO_3 accounts for most, but not all, of the observed CL NO_x monitor interference.

As an added complication, HNO_3 is efficiently lost on stainless steel surfaces (Neuman et al., 1999). The efficiency with which HNO_3 will reach the molybdenum converter within a particular CL NO_x monitor is then dependent on the amount of stainless steel surface area in the inlet manifold, and thus unique to each monitor. Thus, it is not possible to easily extrapolate this result to all CL NO_x monitors. We generally conclude, however, that HNO_3 accounts for a significant portion of the CL NO_x monitor interference.

(d) Alkyl and multifunctional organic nitrates (from hereon referred to as "alkyl nitrates") are known to be produced simultaneously with O_3 from the minor branch (5b) of the reaction of NO with peroxy radicals (Day et al., 2003; Rosen et al., 2004; Trainer et al., 1991).

$$RO_2 + NO \rightarrow NO_2 + RO \quad (5)$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \quad (6)$$

There were no direct measurements of alkyl nitrates as part of the MCMA-2003 campaign of which we are aware. Instead, to study the formation of alkyl nitrates (and HNO_3), we employ a flexible top photochemical box model, which was constrained by measurements conducted at the CENICA supersite for OH sources and sinks from VOC and NO_x. Model simulations were performed with the Master Chemical Mechanism (MCMv3.1) (Jenkin et al., 2003; Saunders et al., 2003) on a 24-hr basis constrained with 10-min averaged measurements of major inorganic species (NO, NO_2, HONO, O_3 and SO_2), CO, 102 volatile organic compounds (VOC), HO_x (=OH+HO_2) measurements, temperature, pressure, water vapor concentration, photolysis frequencies, and dilution. MCMv3.1 is a near-explicit mechanism, i.e. with minimized lumping of VOC reaction pathways, and thus well suited for source-apportionment of organic nitrates and HNO_3 (Sheehy et al., 2006). Figure 3 shows the diurnal profile of the modeled concentrations of alkyl nitrates and HNO_3 from the MCM model. Note that

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the model does not account for horizontal transport and thus modeled concentrations of stable species begin accruing above realistic values after 4 PM local time due to planetary boundary layer dynamics.

Preliminary results from observations from a recent field campaign in 2006 (Farmer et al., 2006) as well as modeling of the outflow of pollution from Mexico City (Madronich, 2006) show that the sum of all alkyl nitrates, ΣAN, comprises roughly (10–30)% of NO_z in the outflow of Mexico City. Additionally, preliminary results from aircraft measurements of alkyl nitrates made during this same field campaign confirm the presence of alkyl nitrates in the outflow from Mexico City (Blake and Atlas, 2006). Alkyl nitrates are thus a non-negligible part of the NO_z budget.

For the locations where measurements of OH and other radicals were not available to constrain the MCM model, we make simple estimates of the alkyl nitrate concentrations based on the measured [O_3]. Using the notation of Day et al. (Day et al., 2003), the branching ratio for the formation of an alkyl nitrate in channel (5b) is defined as α. A general correlation of alkyl nitrates with O_3 is expected because both are photochemically generated in the atmosphere. Subsequent reactions of the alkoxy radical (RO_2) in channel (5a) with O_2 lead to the formation of an HO_2 molecule which reacts to form a second NO_2 molecule, which then produces O_3 via reactions (2) and (3) above. Thus, for each reaction of RO_2 with NO in reaction (5), there is either the formation of one alkyl nitrate or two O_3 molecules. As a result, the slope of a plot of ambient [O_3] versus calculated [ΣAN] is $2(1-\alpha) / \alpha$. We use this relationship to make a simple estimate of [ΣAN] based on the measured [O_3].

We estimate a value for α within Mexico City (α_{MCMA}) based on the measured volatile organic carbon (VOC) speciation. The MCMA-2003 campaign included numerous measurements of the overall VOC loading and speciation thereof (Velasco et al., 2006). Using average speciated VOC concentrations as measured during the campaign and measurements and/or estimates for the branching ratios for channel (5b) of the individual VOC compounds, we calculate α_{MCMA} in a similar manner to the calculations of Rosen et al. (2004) for La Porte, Texas. The ambient VOC mix in Mexico City

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is heavily dominated by propane (29% by volume) and lighter alkanes (≤ C5, 25%), with additional contributions from alkenes (9%), aromatics (8%), heavier alkanes (8%), acetylene (3%) and MTBE (2%), with 15% of the VOC loading left as unidentified. This unidentified portion of the VOC mixture most likely consists of oxygenated VOCs, with branching ratios for reaction (5b) similar to the analogous alkanes and alkenes. We assume a value of α for this unidentified portion of the VOC loading equal to the average of the identified VOCs. We then weight the value of α for each VOC compound by its OH reactivity to determine a best estimate for α_{MCMA} = 0.063. Multiplying the measured [O_3] by this α_{MCMA} gives a time series of the estimated total concentration of alkyl nitrates, [ΣAN], for the various locations in this study. Diurnal profiles of the estimated [ΣAN] are shown in Fig. 3. This simple estimate reveals maxima in [ΣAN] of nearly 5 ppb, which is as large as the largest observed [ΣAN] in other locations (Rosen et al., 2004). Although ambient [VOC] in MCMA are larger than in other urban locations, the MCMA VOC speciation is dominated by light alkanes that do not form alkyl nitrates as readily as longer chain VOCs. For the CENICA supersite, MCM modeled profile of the alkyl nitrates shows a maximum value in the morning, while this simple estimate based on the measured [O_3] shows a peak in afternoon (corresponding the peak in the O_3 concentration). This is likely due to the suppression of O_3 concentrations at the CENICA site during the morning hours due to nearby NO_x sources mentioned earlier. Overall, the simple estimate provides a rough gauge to the magnitude of [ΣAN] expected in a given location.

(e) From the previous sections, we have concluded that HNO_3 and alkyl nitrates contribute to the CL NO_x monitor interference in Mexico City. There is an observable trend in going from "fresh" to "aged" sites, where the contribution of alkyl nitrates relative to the magnitude of the CL NO_x monitor increases moving from the sites in closest proximity to high emissions levels (La Merced and then CENICA) to the sites that are furthest away from large emission sources (Pedregal and then Santa Ana). The estimated [ΣAN] is roughly constant at all locations such that the decreasing magnitude of the CL NO_x monitor interference in going from fresh to aged sites is explained by

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decreasing amounts of HNO_3, i.e., as the air parcel ages, HNO_3 is lost from the gas phase to either particulate nitrate or via dry deposition. If we examine the La Merced (the "freshest" site), the sum of the measured HNO_3 and the estimated ΣAN results in a significantly better agreement of the linear correlation plot (slope = 0.97, R^2=0.53). The diurnal profile shown in Fig. 4 closely matches that of the interference. In summary, we conclude that close to the sources of the emissions, the combination of HNO_3 and ΣAN account for the CL NO_x monitor interference, and as the urban air parcel ages, ΣAN comprises a larger percentage of the interference.

3.2.4 Impact of CL NO_x Monitor Interference

The CL NO_x monitor interference has been shown to account for up to 50% of the measured NO_2 concentration in Mexico City; interferences of this order could impact the non-attainment status of urban areas. The diurnal profile of the CL NO_x monitor interference peaks in the afternoon when NO_2 concentrations are relatively low, impacting annual standards for NO_2, such as those used by Canada and the United States (Demerjian, 2000), more so than daily 1-h maxima standards. For the MCMA-2003 campaign, the averaged NO_2 concentration (the closest comparison to the annual standard we can do with this data) as measured by CL NO_x monitors was higher than co-located spectroscopic techniques by up to 22% at the four sites in this study (see Table 2). For example, the averaged NO_2 concentration measured at La Merced by the CL NO_x monitor was 49.5 ppb versus 40.6 ppb measured by the co-located DOAS instrument; the former measurement comes much closer to the 53 ppb US EPA annually averaged threshold for non-attainment (Environmental Protection Agency, 1993). We note that our maximum observed NO_2 concentration in this study for a 1-h averaged of 185 ppb was significantly lower than the Mexican air quality standard of 210 ppb for a 1-h averaged concentration (Finlayson-Pitts and Pitts, 2000).

Air quality models require uncertainties in NO_2 measurements of roughly ±10%. As such, the observed interferences of up to 50% are unacceptable for the proper evaluation of air quality models (McClenny et al., 2002). In the following section we

make several recommendations for how to avoid and/or account for this interference in the future.

4 Conclusions

It has been shown that high levels of ambient reactive nitrogen species lead to a severe overestimation of ambient NO_2 concentrations by standard chemiluminescence monitors equipped with molybdenum oxide converters. This study is one of the first to quantify this CL NO_x monitor interference and explore its causes in detail. In Mexico City, the observed CL NO_x monitor interference was shown to have no significant contribution from gas phase olefins or ammonia. The good correlation of the CL NO_x monitor interference with ambient O_3 and NO_z concentrations and poor correlation with PAN and particulate nitrate lead to the conclusion that a combination of photochemically produced gas phase nitric acid and alkyl and multifunctional alkyl nitrates is primarily responsible for this interference. The percentage contribution of HNO_3 to the interference decreases as the air parcel moves away from fresh emission sources. Modeling and calculations reveal that ambient alkyl nitrates concentrations in the MCMA are significant, up to several ppb, which is as high as those observed in other urban locations, but plausible given the high VOC loadings in Mexico City. During the MCMA-2003 field campaign, the CL NO_x monitor interference caused the average measured NO_2 concentration to be larger than co-located spectroscopic measurements by up to 22%. This magnitude of interference is inappropriately large for use in modeling studies and may lead to a non-attainment status for NO_2 to be incorrectly assigned in certain urban areas.

In conclusion, we make several recommendations for future studies. (1) We encourage future field campaigns that involve absolute NO_2 concentration measurements to do a side-by-side comparison with a standard chemiluminescence NO_x monitor, particularly those that also include direct measurements of HNO_3 and alkyl nitrate concentrations. Such comparisons would help evaluate nitric acid and alkyl nitrates as the

primary cause of the CL NO_x monitor interference and further quantify this interference. (2) It seems unlikely that a simple hardware insertion could be developed to retrofit the currently used CL NO_x monitors to avoid this measurement interference. However, if (a) other studies can confirm these results and better quantify CL NO_x monitor interference from HNO_3 and ΣAN in other urban locations, and (b) it is possible for an urban area to obtain a good speciated VOC emissions inventory and/or speciated VOC measurements, it could be possible to estimate the magnitude of the CL NO_x monitor interference from measured ambient O_3 levels, which are often readily available; ambient NO_2 measurements as made by the currently used CL NO_x monitors could then be post-corrected. (3) In order to avoid this interference in the long term, instrument manufacturers should pursue low-cost spectroscopic techniques for measuring NO_2, particularly those instruments which have the ability to simultaneously measure multiple compounds, i.e., NO, NO_2 and O_3. The development of instrumentation without chemical interference will significantly improve ambient monitoring networks. It is possible that CL NO_x monitors could then used to detect NO and NO_y, where the combination of a CL monitor and a spectroscopic NO_2 instrument would allow the measurement of NO, NO_2 and NO_z.

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Table 1. Slopes of linear least squares fit of correlation plots of observed CL NO_x monitor interference versus other measured species at series of locations. R^2 values for fits are given in parentheses. All concentrations for correlation plots are 15 min averages and are reported in ppb or equivalent ppb. Maxima, minima, and averages for slopes are listed along with range of R^2 values. Abbreviations: NA = measurement data Not Available at particular location, ID = Insufficient Data available at particular location, ML = data from ARI Mobile Lab in stationary mode, Roof = long path instruments at fixed site locations. Stationary sites are: STA = Santa Ana, PED = Pedregal, MER = La Merced and CEN = CENICA headquarters; see text for description. NO_z, O_3 and HNO_3 are highlighted as showing the best correlations.

Species Correlated with CL NO_x Monitor Interference	ML STA	ML PED	ML MER	ML CEN	Roof CEN	Roof MER	Min	Max	Avg	R^2
PTRMS Olefin Proxy m/z 71	1.19 (0.05)	–1.56 (0.03)	–0.86 (0.03)	ID	NA	NA	–1.56	1.19	–0.41	0.03–0.05
PTRMS Olefin Proxy m/z 43	0.36 (0.12)	–0.2 (0.01)	–0.15 (0.06)	ID	NA	NA	–0.2	0.36	0.00	0.01–0.12
FIS Monitor Total Olefins	NA	NA	NA	–0.13 (0.04)	–0.15 (0.32)	NA	–0.15	–0.13	–0.14	0.04–0.32
NH_3	–0.03 (0.03)	0.34 (0.04)	–0.06 (0.17)	0.14	–0.05 (0.01)	0.49 (0.01)	–0.06	0.49	0.14	0.01–0.17
PAN	NA	NA	NA	ID	4.07 (0.09)	NA			4.07	0.09
AMS Particulate Nitrate	2.44 (0.15)	1.74 (0.12)	–0.44 (0.01)	1.68 (0.01)	0.28 (0.01)	NA	–0.44	2.44	1.14	0.01–0.15
NO_z	**0.54 (0.65)**	**0.66 (0.79)**	**0.44 (0.32)**	**0.49 (0.35)**	**NA**	**NA**	**0.44**	**0.66**	**0.53**	**0.32–0.79**
O_3	**0.06 (0.30)**	**0.09 (0.54)**	**0.09 (0.19)**	**ID**	**0.11 (0.21)**	**0.15 (0.21)**	**0.06**	**0.19**	**0.10**	**0.19–0.54**
HNO_3	**NA**	**NA**	**NA**	**NA**	**NA**	**1.83 (0.44)**			**1.83**	**0.44**

Table 2. Averaged measured NO_2 concentrations for 5 week MCMA-2003 campaign by spectroscopic techniques compared to co-located CL NO_x monitors at 4 locations.

Site	Spectroscopic Instrument	MCMA Campaign Average	CL NO_x Monitor	MCMA Campaign Average	% Difference
La Merced	DOAS-UNAM	40.6	RAMA	49.5	+22%
CENICA	DOAS-1	34.1	CENICA	31.0	–9% [a]; +11%
	DOAS-2	28.0			
Pedregal	TILDAS-ML [b]	27.6	ML [b]	29.4	+7%
			RAMA	30.7	+11%
Santa Ana	TILDAS-ML [b]	3.8	ML [b]	9.1	140%

a = DOAS-1 believed to have larger NO_x concentrations than CENICA rooftop owing to major roadway beneath the light path, see discussion above and (Dunlea et al., 2006).
b = The ARI Mobile Lab visit each location for only a few days, which may not be a representative sample of the average NO_2 concentration at each location.

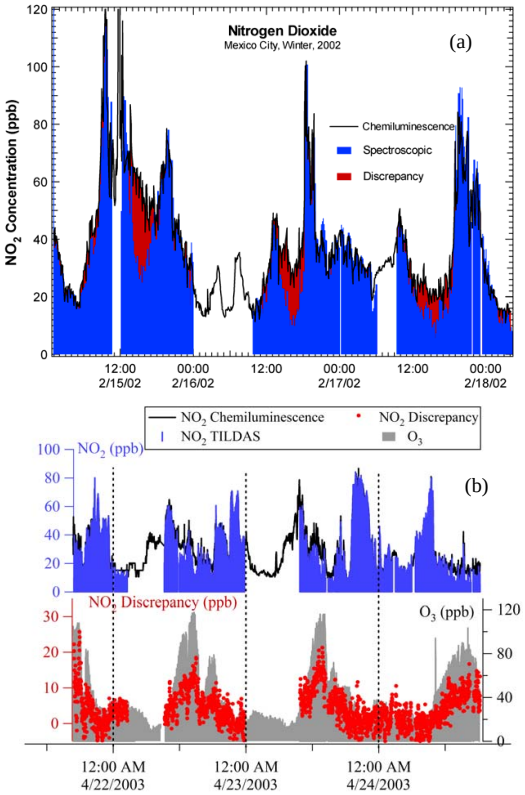

Fig. 1. Panel **(a)** – Time series of NO_2 measurements by standard CL NO_x monitor and TILDAS spectroscopic instruments on board ARI Mobile Lab at the Pedregal fixed monitoring site during 2002 campaign, highlighting periods when the chemiluminescence instrument showed interference. Panel **(b)** – Time series for one-min averaged measurements made on board ARI Mobile Lab at the Pedregal fixed monitoring site during MCMA-2003 field campaign. The CL NO_x monitor interference is plotted on its own axis in this figure to show the correlation in time with ambient O_3 levels, which indicates a photochemical source of the interfering compound(s).

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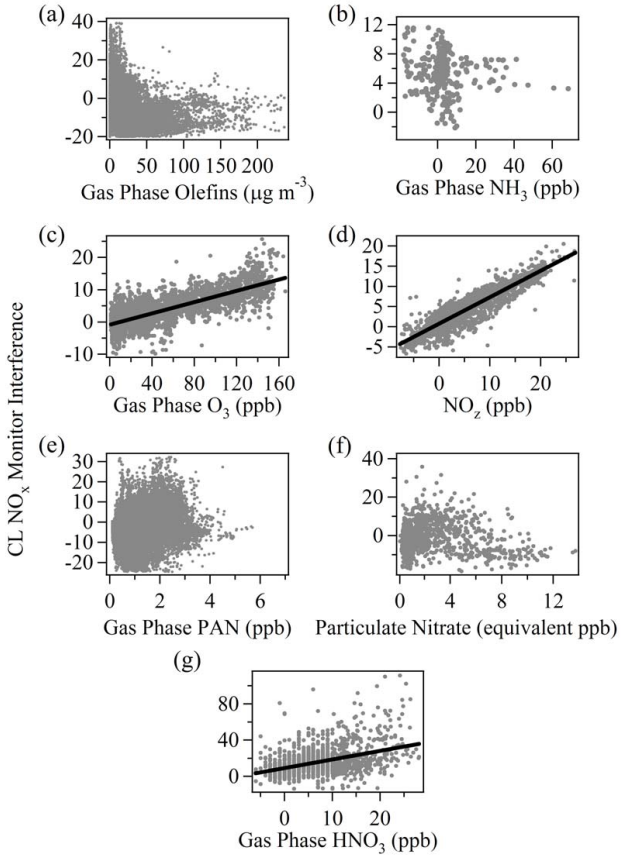

Fig. 2. Linear regression plots for the CL NO_x monitor interference plotted versus **(a)** gas phase olefins (CENICA), **(b)** gas phase NH_3 (Santa Ana), **(c)** gas phase O_3 (Pedregal), **(d)** NO_z (Pedregal), **(e)** gas phase PAN (CENICA), **(f)** particulate nitrate (La Merced), and **(g)** gas phase HNO_3 (La Merced). See text for description of measurements. Results of the linear regressions are listed in Table 1.

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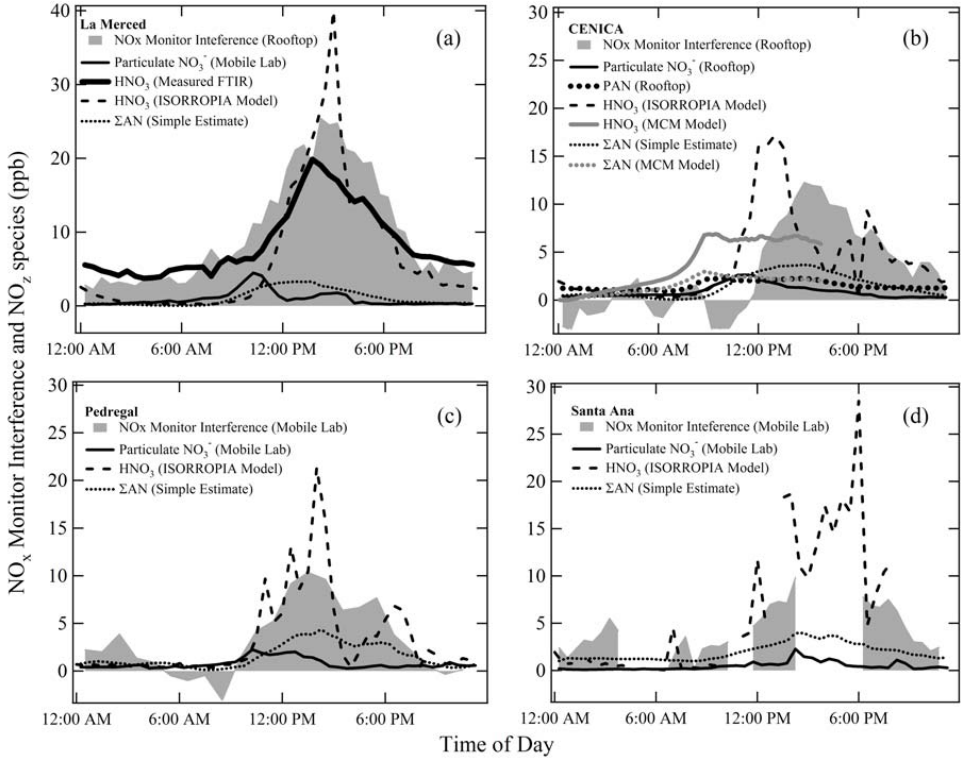

Fig. 3. Diurnally averaged profiles for measured CL NO_x monitor interference, calculated alkyl nitrate concentrations, measured PAN concentrations and measured particulate nitrate in equivalent gas phase concentration as observed at the four fixed sites. Note that only a small fraction of particulate nitrate mass, from particles with diameters <200 nm, could potentially contribute to the NO_x monitor interference. Time of day is for local time. Gaps in profiles are due to limited data.

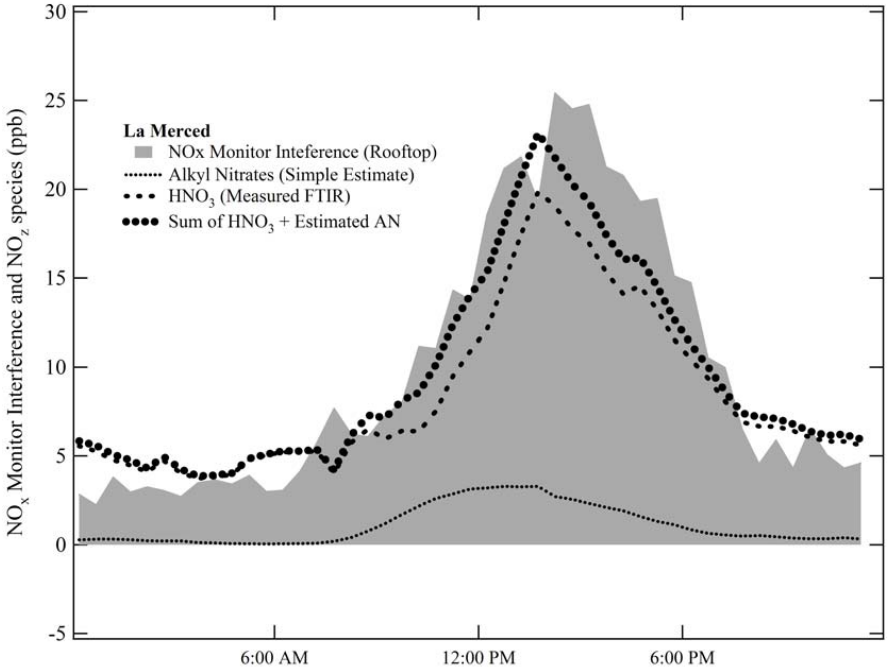

Fig. 4. Diurnally averaged profiles for measured CL NO_x monitor interference, measured HNO_3 concentrations and calculated alkyl nitrate concentrations at La Merced site. Also included is a profile of the sum of the measured HNO_3 concentration plus the estimated alkyl nitrate concentration (see text). Time of day is for local time.

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