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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  $\text{NO}_2$ . Measurements of  $\text{NO}_2$  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  $\text{NO}_2$  concentration during afternoon hours. As expected, this interference correlates well with non- $\text{NO}_x$  reactive nitrogen species ( $\text{NO}_z$ ) as well as with ambient  $\text{O}_3$  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  $\text{HNO}_3$  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  $\text{NO}_x$  monitor interference resulted in an average measured  $\text{NO}_2$  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  $\text{NO}_x$  = sum of nitrogen oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ) are primarily emitted as byproducts of combustion and participate in ozone ( $\text{O}_3$ ) 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<sub>2</sub> is designated as one of the United States Environmental Protection Agency's (US EPA) "criteria pollutants", which also include O<sub>3</sub>, carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), 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<sub>2</sub>, the US EPA has recently announced sweeping new regulations aimed at reducing NO<sub>x</sub> levels by 2015 (Environmental Protection Agency, 2005). Therefore, accurately measuring the concentration of NO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> measurement. In summary, assuring that NO<sub>2</sub> 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<sub>2</sub> concentrations, the most prevalent, and the Federal Reference Method as designated by the US EPA, is the chemiluminescence instrument (CL NO<sub>x</sub> monitors) (Demerjian, 2000). This tech-

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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<sub>3</sub> to form electronically excited NO<sub>2</sub>, 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<sub>3</sub>-generating lamp and a modestly cooled photomultiplier (typically ~ -4°C) are required; thus CL NO<sub>x</sub> 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<sub>x</sub> 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<sub>2</sub> by passing the ambient air stream over a catalyst (usually gold or molybdenum oxide, often heated) to convert NO<sub>2</sub> to NO. The difference of the two values is reported as the NO<sub>2</sub> concentration. Although instruments are available that utilize a flash lamp or laser to convert NO<sub>2</sub> to NO, this study only examines CL NO<sub>x</sub> monitors with molybdenum oxide catalysts, which are the most prevalent type (Parrish and Fehsenfeld, 2000).

In addition to the advantages of CL NO<sub>x</sub> 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<sub>x</sub> monitors is their inability to directly and specifically detect NO<sub>2</sub>. 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<sub>2</sub> by a standard CL NO<sub>x</sub> monitor (Winer et al., 1974). As stated by the US EPA, “chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> 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<sub>2</sub> and valid NO<sub>2</sub> measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known

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or suspected to be high relative to NO<sub>2</sub>, the use of an equivalent method for the measurement of NO<sub>2</sub> is recommended.” (Environmental Protection Agency, 2006) Additionally, manufacturers now use this same technology to make total reactive nitrogen (NO<sub>y</sub>) measurements. Molybdenum oxide catalysts are known to efficiently reduce compounds such as NO<sub>2</sub>, NO<sub>3</sub>, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, CH<sub>3</sub>ONO<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>ONO<sub>2</sub>, n-C<sub>3</sub>H<sub>7</sub>ONO<sub>2</sub>, n-C<sub>4</sub>H<sub>9</sub>ONO<sub>2</sub>, and CH<sub>3</sub>CHONO and to a lesser extent also reduce HO<sub>2</sub>NO<sub>2</sub>, HONO, RO<sub>2</sub>NO<sub>2</sub>, NH<sub>3</sub> and particulate phase nitrate. These catalysts do not efficiently reduce N<sub>2</sub>O, HCN, CH<sub>3</sub>CN or CH<sub>3</sub>NO<sub>2</sub> 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<sub>x</sub> and NO<sub>y</sub> monitors is the position of the catalyst: in a CL NO<sub>y</sub> monitor, the catalyst is placed very close to the front of sampling inlet so as to convert all NO<sub>y</sub> species, whereas in a CL NO<sub>x</sub> monitor, the catalyst is placed after a particulate filter and just before the detection chamber, allowing the conversion and detection as “NO<sub>2</sub>” of any gas phase nitrogen containing compounds not removed by passive loss on surfaces upstream of the converter.

Other more specific NO<sub>2</sub> detection techniques have been developed, including a photolysis technique to specifically convert NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (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<sub>x</sub> 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<sub>x</sub> monitors relative to an absolute TILDAS measurement of NO<sub>2</sub>. 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<sub>2</sub> (de Foy et al., 2005; Molina and Molina, 2006). Here, we utilize this unique data set to evaluate the performance of standard CL NO<sub>x</sub> 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

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(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<sub>2</sub> instrument and a standard CL NO<sub>x</sub> monitor. The TILDAS technique for measuring NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>v<sub>2</sub> wavelength region (1600 cm<sup>-1</sup>), the next strongest absorber (CH<sub>4</sub>) has nearby absorption lines which are six orders of magnitude weaker than the NO<sub>2</sub> lines used in these measurements. Additionally, the CH<sub>4</sub> lines are frequency shifted away from the main NO<sub>2</sub> features and this is resolved with the typical linewidth of the lead salt diode lasers used. Therefore, the measurements of NO<sub>2</sub> by tunable diode laser spectroscopy are believed to be interference-free. The mode purity of the diode was verified by measuring ‘black’ NO<sub>2</sub> 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

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in the two instrument channels, measuring NO and NO<sub>2</sub> respectively, the presently accepted band strengths are known to within 6% for NO and 4% for NO<sub>2</sub> (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<sub>2</sub> measurements.

Standard CL NO<sub>x</sub> 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<sub>x</sub>-free air and then adding several specified amounts of NO to the instrument covering the desired operating range. The CL NO<sub>x</sub> 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<sub>2</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>2</sub> amongst a suite of other compounds. The detection limits for NO<sub>2</sub> 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<sub>3</sub>; detection limit of 4 ppb) and from the DOAS measurement

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of NO<sub>2</sub> (detection limit of 3 ppb) are shown here.

### 3 Results and Discussions

#### 3.1 Observation of Interference

Simultaneous measurements of NO<sub>2</sub> on board the ARI Mobile Lab by the CL NO<sub>x</sub> monitor and the TILDAS instrument revealed a recurring discrepancy where the CL NO<sub>x</sub> monitor reported a higher NO<sub>2</sub> 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<sub>x</sub> monitor interference” as the CL NO<sub>x</sub> monitor NO<sub>2</sub> measurement minus a co-located spectroscopic NO<sub>2</sub> measurement.

$$\text{CLNO}_x\text{ monitor interference} = [\text{NO}_2](\text{CL monitor}) - [\text{NO}_2](\text{spectroscopic}) \quad (1)$$

Figure 1 shows the CL NO<sub>x</sub> monitor interference as observed during both the 2002 and 2003 field campaigns. The CL NO<sub>x</sub> monitor interference was observed to occur daily, peaking in the afternoons during periods when ambient O<sub>3</sub> levels were highest. The CL NO<sub>x</sub> monitor interference accounted for as much as 50% of the total NO<sub>2</sub> concentration reported by the CL NO<sub>x</sub> 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<sub>2</sub> levels at the boundary site. Additionally, this CL NO<sub>x</sub> monitor interference was present when comparing DOAS long path measurements of NO<sub>2</sub> to CL NO<sub>x</sub> monitors at both the CENICA and La Merced sites. For these sites, the CL NO<sub>x</sub> 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

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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<sub>x</sub> 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<sub>x</sub> monitor interference was observed to occur regularly and to roughly correlate with the ambient O<sub>3</sub> 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<sub>2</sub> 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<sub>x</sub> fraction of reactive nitrogen (NO<sub>z</sub>).

#### 3.2.1 Gas Phase Olefins

The chemiluminescent reaction of ambient gas phase olefins with excess O<sub>3</sub> within the CL NO<sub>x</sub> monitor reaction chamber, where the resulting fluorescence is recorded as NO<sub>2</sub>, is a potential interference to the CL NO<sub>x</sub> monitor. However, no correlation of the measured CL NO<sub>x</sub> 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/z*43 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<sub>3</sub> (Velasco et al., 2006). Both the PTRMS and the FIS measured olefin levels were high enough to potentially account for the CL NO<sub>x</sub> monitor interference, however, neither measurement correlated in time with the interference.

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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<sub>x</sub> monitor interference. Based on these observations, we conclude that gas phase olefins did not contribute significantly to the observed CL NO<sub>x</sub> monitor interference.

### 3.2.2 Gas Phase Ammonia

A second possibility for the cause of the CL NO<sub>x</sub> monitor interference is gas phase ammonia (NH<sub>3</sub>), 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<sub>3</sub> and the CL NO<sub>x</sub> monitor interference. Measured ambient NH<sub>3</sub> concentrations were typically less than 30 ppb (and only very rarely exceeded 100 ppb), translating to potential interferences in the chemiluminescence NO<sub>2</sub> measurement on the order of less than 3 ppb, not enough to account for the regularly observed interferences around 10–20 ppb. Additionally, NH<sub>3</sub> 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<sub>x</sub> 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<sub>x</sub> monitor interference versus the measured NH<sub>3</sub> concentrations were less than 0.34 and R<sup>2</sup> values did not exceed 0.17, indicating no significant correlation (see Table 1). We conclude that gas phase NH<sub>3</sub> did not contribute significantly to the observed CL NO<sub>x</sub> monitor interference.

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### 3.2.3 The Non-NO<sub>x</sub> Fraction of Reactive Nitrogen (NO<sub>z</sub>)

It has been long established that molybdenum converters within standard CL NO<sub>x</sub> monitors have a potential interference in the NO<sub>2</sub> 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<sub>y</sub> instrument (TECO 49C), which measures both NO<sub>y</sub> and NO using the chemiluminescence technique, but configured differently than a standard CL NO<sub>x</sub> monitor so as to purposely exploit the molybdenum converter's ability to detect more gas phase reactive nitrogen species. From the CL NO<sub>y</sub> monitor NO<sub>y</sub> and NO measurements, along with the TILDAS NO<sub>2</sub> measurement, we calculated the non-NO<sub>x</sub> fraction of NO<sub>y</sub>, referred to as NO<sub>z</sub>. Table 1 lists the results of linear least-squares fits of the correlation plots of the CL NO<sub>x</sub> monitor interference versus NO<sub>z</sub> at the various locations visited by the ARI Mobile Lab. The CL NO<sub>x</sub> monitor interference level varied linearly with the NO<sub>z</sub> concentration, and was smaller in magnitude, indicating that some portion of NO<sub>z</sub> was responsible for the interference. Fair to good correlation ( $R^2 = 0.32\text{--}0.79$ ) was observed at all sites visited by the ARI Mobile Lab, with ratios of the CL NO<sub>x</sub> monitor interference to NO<sub>z</sub> = (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<sub>x</sub> monitor interference.

This type of comparison has a number of inherent limitations. Negative values for the CL NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> monitor interference measurements indicating that the open

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path DOAS light paths may be influenced by NO<sub>x</sub> 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<sub>2</sub> measurement in more detail.

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

We now examine the individual species that make up NO<sub>2</sub> in order to determine the most likely contributors to the CL NO<sub>x</sub> 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 ( $\text{NO}_3$ ) and  $\text{N}_2\text{O}_5$ . 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  $\text{NO}_x$  monitor interferences. Lastly, measured concentrations of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  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 ( $\text{pNO}_3^-$ ) may be converted by the CL  $\text{NO}_x$  monitor and reported as  $\text{NO}_2$  if sufficiently small particles can penetrate the particulate filter on the CL  $\text{NO}_x$  monitor. The particulate filter on a CL  $\text{NO}_x$  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  $1.0 \mu\text{m}$ , including  $\text{pNO}_3^-$ . 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  $<200 \text{ nm}$ , (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  $\text{pNO}_3^-$ , only a small fraction would be expected to enter a CL  $\text{NO}_x$  monitor resulting in a potential interference.

Diurnal profiles of  $\text{pNO}_3^-$  (Fig. 3) show that concentrations of submicron  $\text{pNO}_3^-$  (as converted to its equivalent gas phase concentration) observed in Mexico City were significantly smaller than the CL  $\text{NO}_x$  monitor interference. At all sites and times, a minimum of 150% of the measured submicron  $\text{pNO}_3^-$  would be required to explain all of the  $\text{NO}_2$  interference. Particulate nitrate from particles with diameters  $<200 \text{ nm}$  is therefore negligible compared to the CL  $\text{NO}_x$  monitor interference. Additionally, the

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diurnal profiles in Fig. 3 show that the maximum in pNO<sub>3</sub> occurs in the morning, a few hours before the maximum in the CL NO<sub>x</sub> monitor interference. Table 1 reports only a weak correlation ( $R^2 < 0.15$ ) of the CL NO<sub>x</sub> monitor interference with the measured ambient submicron pNO<sub>3</sub><sup>-</sup> levels for all sites. Overall, it is clear that pNO<sub>3</sub><sup>-</sup> does not contribute significantly to the observed CL NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> monitor interference versus the measured PAN concentrations on the CENICA rooftop show an  $R^2 = 0.09$ . PAN and similar peroxyacetyl nitrate compounds are therefore concluded to not contribute significantly to the observed CL NO<sub>x</sub> 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 peroxyacetyl nitrate compounds can account for a significant fraction of the NO<sub>2</sub> 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<sub>3</sub>) is photochemically produced within urban atmospheres and has been observed in significant concentrations in Mexico City (Moya et al., 2004). Production of HNO<sub>3</sub> is generally on the same time scale as production of O<sub>3</sub>, since both involve the formation of NO<sub>2</sub>. O<sub>3</sub> is formed when NO<sub>2</sub> photolyzes via a two step process:





(where M represents a third body colliding molecule, presumably  $\text{N}_2$  or  $\text{O}_2$ ).  $\text{HNO}_3$  is formed from the association reaction of OH with  $\text{NO}_2$



5 The formation of  $\text{HNO}_3$  is thus dependent on the competition between reactions (2) and (4). The measured concentrations of  $\text{NO}_2$  and OH during MCMA-2003 (Volkamer et al., 2005) indicate that  $\text{HNO}_3$  production rates via reaction (4) are quite large ( $>15$  ppb  $\text{hr}^{-1}$  at maximum). However, losses for  $\text{HNO}_3$  within an urban area are also significant, and the ambient concentration depends on the balance between the production and  
10 loss rates. In the presence of  $\text{NH}_3$ ,  $\text{HNO}_3$  will readily form particle phase ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).  $\text{HNO}_3$  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 ( $4\text{--}26$   $\text{cm s}^{-1}$ ) 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  $\text{HNO}_3$  as much  
15 as possible. During the MCMA-2003 campaign, the only direct  $\text{HNO}_3$  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  $\text{HNO}_3$  concentrations show reasonably good correlation with the CL  $\text{NO}_x$  monitor interference concentrations ( $R^2=0.44$ ), the slope of the correlation plot (1.41) indicates that  $\text{HNO}_3$   
20 accounts for  $\sim 60\%$  of the CL  $\text{NO}_x$  monitor interference.

For the locations that did not have a measurement of  $\text{HNO}_3$ , we use modeled values to estimate the possible contribution of  $\text{HNO}_3$  to the CL  $\text{NO}_x$  monitor. San Martini et al. (San Martini et al., 2006a; 2006b) have used an ISORROPIA model embedded in  
25 a Markov Chain Monte Carlo algorithm to analyze aerosol data and to predict the gas phase  $\text{HNO}_3$  concentrations at the locations included in this study. Diurnal profiles of these predicted  $\text{HNO}_3$  concentrations are included in Fig. 3. In general,  $\text{HNO}_3$  levels are shown to be large enough to account for the measured CL  $\text{NO}_x$  monitor interference. However, we note that the measured  $\text{HNO}_3$  concentrations at La Merced are

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lower than the predicted levels. We therefore generally conclude that HNO<sub>3</sub> accounts for most, but not all, of the observed CL NO<sub>x</sub> monitor interference.

As an added complication, HNO<sub>3</sub> is efficiently lost on stainless steel surfaces (Neuman et al., 1999). The efficiency with which HNO<sub>3</sub> will reach the molybdenum converter within a particular CL NO<sub>x</sub> 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<sub>x</sub> monitors. We generally conclude, however, that HNO<sub>3</sub> accounts for a significant portion of the CL NO<sub>x</sub> monitor interference.

(d) Alkyl and multifunctional organic nitrates (from hereon referred to as “alkyl nitrates”) are known to be produced simultaneously with O<sub>3</sub> 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).



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<sub>3</sub>), 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<sub>x</sub>. 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<sub>2</sub>, HONO, O<sub>3</sub> and SO<sub>2</sub>), CO, 102 volatile organic compounds (VOC), HO<sub>x</sub> (=OH+HO<sub>2</sub>) 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<sub>3</sub> (Sheehy et al., 2006). Figure 3 shows the diurnal profile of the modeled concentrations of alkyl nitrates and HNO<sub>3</sub> 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,  $\Sigma\text{AN}$ , comprises roughly (10–30)% of  $\text{NO}_2$  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  $\text{NO}_2$  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  $[\text{O}_3]$ . 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  $\alpha$ . A general correlation of alkyl nitrates with  $\text{O}_3$  is expected because both are photochemically generated in the atmosphere. Subsequent reactions of the alkoxy radical ( $\text{RO}_2$ ) in channel (5a) with  $\text{O}_2$  lead to the formation of an  $\text{HO}_2$  molecule which reacts to form a second  $\text{NO}_2$  molecule, which then produces  $\text{O}_3$  via reactions (2) and (3) above. Thus, for each reaction of  $\text{RO}_2$  with NO in reaction (5), there is either the formation of one alkyl nitrate or two  $\text{O}_3$  molecules. As a result, the slope of a plot of ambient  $[\text{O}_3]$  versus calculated  $[\Sigma\text{AN}]$  is  $2(1-\alpha) / \alpha$ . We use this relationship to make a simple estimate of  $[\Sigma\text{AN}]$  based on the measured  $[\text{O}_3]$ .

We estimate a value for  $\alpha$  within Mexico City ( $\alpha_{\text{MCMA}}$ ) 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  $\alpha_{\text{MCMA}}$  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 ( $\leq C_5$ , 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  $\alpha$  for this unidentified portion of the VOC loading equal to the average of the identified VOCs. We then weight the value of  $\alpha$  for each VOC compound by its OH reactivity to determine a best estimate for  $\alpha_{\text{MCMA}} = 0.063$ . Multiplying the measured  $[O_3]$  by this  $\alpha_{\text{MCMA}}$  gives a time series of the estimated total concentration of alkyl nitrates,  $[\Sigma\text{AN}]$ , for the various locations in this study. Diurnal profiles of the estimated  $[\Sigma\text{AN}]$  are shown in Fig. 3. This simple estimate reveals maxima in  $[\Sigma\text{AN}]$  of nearly 5 ppb, which is as large as the largest observed  $[\Sigma\text{AN}]$  in other locations (Rosen et al., 2004). Although ambient  $[\text{VOC}]$  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  $\text{NO}_x$  sources mentioned earlier. Overall, the simple estimate provides a rough gauge to the magnitude of  $[\Sigma\text{AN}]$  expected in a given location.

(e) From the previous sections, we have concluded that  $\text{HNO}_3$  and alkyl nitrates contribute to the CL  $\text{NO}_x$  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  $\text{NO}_x$  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  $[\Sigma\text{AN}]$  is roughly constant at all locations such that the decreasing magnitude of the CL  $\text{NO}_x$  monitor interference in going from fresh to aged sites is explained by

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decreasing amounts of  $\text{HNO}_3$ , i.e., as the air parcel ages,  $\text{HNO}_3$  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  $\text{HNO}_3$  and the estimated  $\Sigma\text{AN}$  results in a significantly better agreement of the linear correlation plot (slope = 0.97,  $R^2=0.53$ ).

5 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  $\text{HNO}_3$  and  $\Sigma\text{AN}$  account for the CL  $\text{NO}_x$  monitor interference, and as the urban air parcel ages,  $\Sigma\text{AN}$  comprises a larger percentage of the interference.

### 3.2.4 Impact of CL $\text{NO}_x$ Monitor Interference

10 The CL  $\text{NO}_x$  monitor interference has been shown to account for up to 50% of the measured  $\text{NO}_2$  concentration in Mexico City; interferences of this order could impact the non-attainment status of urban areas. The diurnal profile of the CL  $\text{NO}_x$  monitor interference peaks in the afternoon when  $\text{NO}_2$  concentrations are relatively low, impacting annual standards for  $\text{NO}_2$ , 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  $\text{NO}_2$  concentration (the closest comparison to the annual standard we can do with this data) as measured by CL  $\text{NO}_x$  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  $\text{NO}_2$  concentration measured at La Merced by the CL  $\text{NO}_x$  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  $\text{NO}_2$  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).

25 Air quality models require uncertainties in  $\text{NO}_2$  measurements of roughly  $\pm 10\%$ . 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

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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  $\text{NO}_2$  concentrations by standard chemiluminescence monitors equipped with molybdenum oxide converters. This study is one of the first to quantify this CL  $\text{NO}_x$  monitor interference and explore its causes in detail. In Mexico City, the observed CL  $\text{NO}_x$  monitor interference was shown to have no significant contribution from gas phase olefins or ammonia. The good correlation of the CL  $\text{NO}_x$  monitor interference with ambient  $\text{O}_3$  and  $\text{NO}_z$  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  $\text{HNO}_3$  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  $\text{NO}_x$  monitor interference caused the average measured  $\text{NO}_2$  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  $\text{NO}_2$  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  $\text{NO}_2$  concentration measurements to do a side-by-side comparison with a standard chemiluminescence  $\text{NO}_x$  monitor, particularly those that also include direct measurements of  $\text{HNO}_3$  and alkyl nitrate concentrations. Such comparisons would help evaluate nitric acid and alkyl nitrates as the

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primary cause of the CL NO<sub>x</sub> 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<sub>x</sub> monitors to avoid this measurement interference. However, if (a) other studies can confirm these results and better quantify CL NO<sub>x</sub> monitor interference from HNO<sub>3</sub> 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<sub>x</sub> monitor interference from measured ambient O<sub>3</sub> levels, which are often readily available; ambient NO<sub>2</sub> measurements as made by the currently used CL NO<sub>x</sub> 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<sub>2</sub>, particularly those instruments which have the ability to simultaneously measure multiple compounds, i.e., NO, NO<sub>2</sub> and O<sub>3</sub>. The development of instrumentation without chemical interference will significantly improve ambient monitoring networks. It is possible that CL NO<sub>x</sub> monitors could then be used to detect NO and NO<sub>y</sub>, where the combination of a CL monitor and a spectroscopic NO<sub>2</sub> instrument would allow the measurement of NO, NO<sub>2</sub> and NO<sub>z</sub>.

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## References

- Beauchamp, J., Wisthaler, A., Grabner, W., Neuner, C., Weber, A., and Hansel, A.: Short-term measurements of CO, NO, NO<sub>2</sub>, organic compounds and PM<sub>10</sub> at a motorway location in an Austrian valley, *Atmos. Env.*, 38, 2511–2522, 2004.
- Blake, D. and Atlas, E.: Personal Communication, 2006.

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- Carslaw, D. C. and Beevers, S. D.: Investigating the potential importance of primary NO<sub>2</sub> emissions in a street canyon, *Atmos. Env.*, 38, 3585–3594, 2004.
- Carslaw, D. C. and Beevers, S. D.: Estimations of road vehicel primary NO<sub>2</sub> exhaust emission fractions using monitoring data in London, *Atmos. Env.*, 39, 167–177, 2005.
- 5 Cavanagh, R. R. and Verkouteren, R. M.: Improving the Scientific Basis for Informed Decisions on Atmospheric Issues, NIST-NOAA-Industry Workshop on Atmospheric Measures and Standards, National Institute of Standards and Technology, 2001.
- Day, D. A., Dillon, M. B., Wooldridge, P. J., Thornton, J. A., Rosen, R. S., Wood, E. C., and Cohen, R. C.: On alkyl nitrates, O<sub>3</sub>, and the “missing NO<sub>y</sub>”, *J. Geophys. Res.*, 108, D16, 4501, 2003.
- 10 de Foy, B., Caetano, E., Magaña, V., Zitácuaro, A., Cardenas, B., Retama, A., Ramos, R., Molina, L. T., and Molina, M. J.: Mexico City basin wind circulation during the MCMA-2003 field campaign, *Atmos. Chem. Phys.*, 5, 2267–2288, 2005.
- Demerjian, K. L.: A review of national monitoring networks in North America, *Atmos. Env.*, 34, 1861–1884, 2000.
- 15 Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., Lamb, B. K., Allwine, E. J., Grutter, M., Villegas, C. R. R., Marquez, C., Blanco, S., Cardenas, B., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of Standard Ultraviolet Absorption Ozone Monitors in a Polluted Urban Environment, *Atmos. Chem. Phys.*, 6, 3163–3180, 2006.
- 20 Environmental Protection Agency, U. S.: Air Quality Criteria for Oxides of Nitrogen, Office of Research and Development, [http://www.epa.gov/ttn/naaqs/standards/nox/s\\_nox\\_index.html](http://www.epa.gov/ttn/naaqs/standards/nox/s_nox_index.html), 1993.
- Environmental Protection Agency, U. S.: Recommended Methods for Ambient Air Monitoring of NO, NO<sub>2</sub>, NO<sub>y</sub>, and Individual NO<sub>z</sub> Species, National Exposure Research Laboratory, 2001.
- 25 Environmental Protection Agency, U. S.: US EPA Audit of RAMA Network, [http://www.sma.df.gob.mx/sma/download/archivos/auditoria\\_epa\\_ingles.pdf](http://www.sma.df.gob.mx/sma/download/archivos/auditoria_epa_ingles.pdf), 2003.
- Environmental Protection Agency, U. S.: National Ambient Air Monitoring Strategy, Office of Air Quality Planning and Standards, <http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/naamstrat2005.pdf>, 2005.
- 30 Environmental Protection Agency, U. S.: Electronic Code of Federal Regulations, <http://www.gpoaccess.gov/cfr/index.html>, 2006.
- Farmer, D. K., Wooldridge, P. J., and Cohen, R. C.: Personal Communication, 2006.
- Fehsenfeld, F. C., Dickerson, R. R., Hubler, G., Luke, W. T., Nunnermacker, L. J., Williams,

---

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E. J., Roberts, J. M., Calvert, J. G., Curran, C. M., Delany, A. C., Eubank, C. S., Fahey, D. W., Fried, A., Gandrud, B. W., Langford, A. O., Murphy, P. C., Norton, R. B., Pickering, K. E., and Ridley, B. A.: A Ground-Based Intercomparison of NO, NO<sub>x</sub>, and NO<sub>y</sub> Measurement Techniques, *J. Geophys. Res.*, 92, D12, 14 710–14 722, 1987.

5 Fehsenfeld, F. C., Drummand, J. W., Roychowdhury, U. K., Galvin, P. J. W., E.J., Burh, M. P., Parrish, D. D., Hubler, G., Langford, A. O., Calvert, J. G., Ridley, B. A., Grahek, F., Heikes, B. G., Kok, G. L., Shetter, J. D., Walega, J. G., Elsworth, C. M., Norton, R. B., Fahey, D. W., Murphy, P. C., Hovermale, C., Mohnen, V. A., Demerjian, K. L., Mackay, G. I., and Schiff, H. I.: Intercomparison of NO<sub>2</sub> Measurement Techniques, *J. Geophys. Res.*, 95, D4, 3579–3597, 1990.

10 Finlayson-Pitts, B. J. and Pitts, J. N.: *Chemistry of the Upper and Lower Atmosphere*, Academic Press, 2000.

Flores, E., Grutter, M., Galle, B., Mellqvist, J., Samuelsson, J., Knighton, B., Jobson, B. T., Volkamer, R., Molina, L. T., and Molina, M. J., American Geophysical Union Fall Meeting, EOS Trans., 85 (47), Abstract A11A-0003, 2004.

15 Fontijn, A., Sabadell, A. J., and Ronco, R. J.: Homogeneous chemiluminescence measurement of nitric oxide with ozone, *Anal. Chem.*, 42, 575–579, 1970.

Friedeburg, C. v., Pundt, I., Mettendorf, K.-U., Wagner, T. and Platt, U.: Multi-axis-DOAS measurements of NO<sub>2</sub> during the BAB II motorway emission campaign, *Atmos. Env.*, 39, 977–985, 2005.

20 Gaffney, J. S., Marley, N. A., Cunningham, M. M., and Doskey, P. V.: Measurements of peroxyacyl nitrates (PANS) in Mexico City: implications for megacity air quality impacts on regional scales, *Atmos. Env.*, 33, 30, 5003–5012, 1999.

Gregory, G. L., Hoell, J. M., Carroll, M. A., Ridley, B. A., Davis, D. D., Bradshaw, J., Rodgers, M. O., Sandholm, S. T., Schiff, H. I., Hastie, D. R., Karecki, D. R., Mackay, G. I., Harris, G. W., Torres, A. L., and Fried, A.: An Intercomparison of Airborne Nitrogen Dioxide Instruments, *J. Geophys. Res.*, 95, D7, 10 103–10 127, 1990.

25 Grutter, M.: Multi-Gas analysis of ambient air using FTIR spectroscopy over Mexico City, *Atmosfera*, 16, 1, 1–13, 2003.

30 Herndon, S. C., Jayne, J. T., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Alwine, E., Lamb, B., Zavala, M., Nelson, D. D., McManus, B., Shorter, J. H., Canagaratna, M. R., Onasch, T. B. and Kolb, C. E.: Characterization of urban pollutant emission fluxes and ambient concentration distributions using a mobile laboratory with rapid response instrumentation, *Faraday*

- Discuss., 130, 327–339, 2005.
- Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, *Aerosol Science and Technology*, 33, 1–2, 49–70, 2000.
- 5 Jenkin, M. E.: Analysis of sources and partitioning of oxidant in the UK - Part 2: contributions of nitrogen dioxide emissions and background ozone at a kerbside location in London, *Atmos. Env.*, 38, 5131–5138, 2004a.
- Jenkin, M. E.: Analysis of sources and partitioning of oxidant in the UK—Part 1: the NO<sub>x</sub>-dependence of annual mean concentrations of nitrogen dioxide and ozone, *Atmos. Env.*, 38, 5117–5129, 2004b.
- 10 Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 181–193, 2003.
- Jimenez, J. L., McCrae, G. J., Nelson, D. D., Zahniser, M. S., and Kolb, C. E.: Remote Sensing of NO and NO<sub>2</sub> Emissions from Heavy-Duty Diesel Trucks Using Tunable Diode Lasers, *Env. Sci. & Tech.*, 34, 12, 2380–2387, 2000.
- 15 Kebabian, P. L., Herndon, S. C., and Freedman, A.: Detection of Nitrogen Dioxide by Cavity Attenuated Phase Shift Spectroscopy, *Anal. Chem.*, 77, 724–728, 2005.
- Kley, D. and McFarland, M.: Chemiluminescence detector for NO and NO<sub>2</sub>, *Atmos. Tech.*, 12, 63–69, 1980.
- 20 Kolb, C. E., Herndon, S. C., McManus, J. B., Shorter, J. H., Zahniser, M. S., Nelson, D. D. J., Jayne, J. T., Canagaratna, M. R., and Worsnop, D. R.: Mobile Laboratory with Rapid Response Instruments for Real-Time Measurements of Urban and Regional Trace Gas and Particulate Distributions and Emission Source Characteristics, *Env. Sci. & Tech.*, 38, 5694–5703, 2004.
- 25 Latham, S., Kollamthodi, S., Boulter, P. G., Nelson, P. M., and Hickman, A. J.: Assessment of primary NO<sub>2</sub> emissions, hydrocarbon speciation and particulate sizing on a range of road vehicles, Report PR/SE/353/2001, 3–7, Transport Research Laboratory (TRL), 2001.
- Li, Y. Q., Demerjian, K. L., Zahniser, M. S., Nelson, D. D., McManus, J. B., and Herndon, S. C.: Measurement of formaldehyde, nitrogen dioxide, and sulfur dioxide at Whiteface Mountain using a dual tunable diode laser system, *J. Geophys. Res.*, 109, D16S08, 2004.
- 30 Madronich, S.: Chemical evolution of gaseous air pollutants down-wind of tropical megacities: Mexico City case study, *Atmos. Env.*, 40, 6012–6018, 2006.

---

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Marley, N. A., Gaffney, J. S., White, R. V., Rodriguez-Cuadra, L., Herndon, S. C., Kolb, C. E., Dunlea, E. J., Volkamer, R. M., Molina, L. T., and Molina, M. J.: Fast Gas Chromatography with Luminol Chemiluminescent Detection for the Simultaneous Determination of Nitrogen Dioxide (NO<sub>2</sub>) and Peroxyacetyl Nitrate (PAN) in the Atmosphere, *Rev. Sci. Inst.*, 75, 4595–4605, 2004.

McClenny, W. A., Williams, E. J., Cohen, R. C., and Stutz, J.: Preparing to Measure the Effects of the NO<sub>x</sub> SIP Call - Methods for Ambient Air Monitoring of NO, NO<sub>2</sub>, NO<sub>y</sub>, and Individual NO<sub>z</sub> Species, *J. Air & Waste Manage. Assoc.*, 52, 542–562, 2002.

McManus, J. B., Kebabian, P. L., and Zahniser, M. S.: Astigmatic mirror multiple pass absorption cells for long pathlength spectroscopy, *Appl. Opt.*, 34, 3336–3348, 1995.

Molina, L. T. and Molina, M. J.: Air Pollution in Megacities, <http://mce2.org/fc03/fc03.html>, 2006.

Moya, M., Grutter, M., and Baez, A.: Diurnal variability of size-differentiated inorganic aerosols and their gas-phase precursors during January and February of 2003 near downtown Mexico City, *Atmos. Env.*, 38, 5651–5661, 2004.

Neuman, J. A., Huey, L. G., Ryerson, T. B., and Fahey, D. W.: Study of Inlet Materials for Sampling Atmospheric Nitric Acid, *Env. Sci. & Tech.*, 33, 1133–1136, 1999.

Neuman, J. A., Parrish, D. D., Ryerson, T. B., Brock, C. A., Wiedinmyer, C., Frost, G. J., Holloway, J. S., and Fehsenfeld, F. C.: Nitric acid loss rates measured in power plant plumes, *J. Geophys. Res.-Atm.*, 109, D23, D23304, 2004.

Parrish, D. D. and Fehsenfeld, F. C.: Methods for gas-phase measurements of ozone, ozone precursors and aerosol precursors, *Atmos. Env.*, 34, 1921–1957, 2000.

Platt, U.: Chapter 2, Sigrist, M. W., *Monitoring by Spectroscopic Techniques*, Wiley & Sons, 1994.

Platt, U. and Perner, D.: Direct Measurements of Atmospheric CH<sub>2</sub>O, HNO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub> and SO<sub>2</sub> by Differential Optical Absorption in the Near UV, *J. Geophys. Res.*, 85, 7453–7458, 1980.

Pundt, I., Mettendorf, K.-U., Laepple, T., Knab, V., Xie, P., Losch, J., Friedeburg, C. v., Platt, U., and Wagner, T.: Measurements of trace gas distributions using Long-path DOAS-Tomography during the motorway campaign BAB II: experimental setup and results for NO<sub>2</sub>, *Atmos. Env.*, 39, 967–975, 2005.

RAMA: Red Automatica de Monitoreo Atmosferico, <http://www.sma.df.gob.mx/simat/pnrama2.htm>, 2005.

---

## Evaluation of NO<sub>2</sub> Chemiluminescence Monitors

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- Ridley, B. A. and Howlett, L. C.: An instrument for nitric oxide measurements in the stratosphere, *Rev. Sci. Instr.*, 45, 742–746, 1974.
- Rogers, T. M., Grimsrud, E. P., Herndon, S. C., Jayne, J. T., Kolb, C. E., Allwine, E., Westberg, H., Lamb, B. K., Zavala, M., Molina, L. T., Molina, M. J., and Knighton, W. B.: On-road measurement of volatile organic compounds in the Mexico City metropolitan area using proton transfer reaction mass spectrometry, *Int. J. of Mass Spec.*, 252, 26–37, 2006.
- Rosen, R. S., Wood, E. C., Wooldridge, P. J., Thornton, J. A., Day, D. A., Kuster, W., Williams, E. J., Jobson, B. T., and Cohen, R. C.: Observations of total alkyl nitrates during Texas Air Quality Study 2000: Implications for O<sub>3</sub> and alkyl nitrate photochemistry, *J. Geophys. Res.*, 109, D07303, doi:10.1029/2003JD004227, 2004.
- Rothman, L. S., Barbe, A., Benner, D. C., Brown, L. R., Camy-Peyret, C., Carleer, M. R., Chance, K., Clerbaux, C., Dana, V., Devi, V. M., Fayt, A., Flaud, J. M., Gamache, R. R., Goldman, A., Jacquemart, D., Jucks, K. W., Lafferty, W. J., Mandin, J. Y., Massie, S. T., Nemtchinov, V., Newnham, D. A., Perrin, A., Rinsland, C. P., Schroeder, J., Smith, K. M., Smith, M. A. H., Tang, K., Toth, R. A., Vander Auwera, J., Varanasi, P., and Yoshino, K.: The HITRAN molecular spectroscopic database: edition of 2000 including updates through 2001, *J. Quant. Spectros. Radiat. Transfer*, 82, 5–44, 2003.
- Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabe, R. M., Marquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Leshner, R., Shirley, T., and Jimenez, J. L.: Characterization of Ambient Aerosols in Mexico City during the MCMA-2003 Campaign with Aerosol Mass Spectrometry: Results at the CENICA Supersite, *Atmos. Chem. Phys.*, 6, 925–946, 2006.
- San Martini, F. M., Dunlea, E. J., Grutter, M., Onasch, T. B., Jayne, J. T., Canagaratna, M. R., Worsnop, D. R., Kolb, C. E., Shorter, J. H., Herndon, S. C., Zahniser, M. S., Ortega, J. M., McRae, G. J., Molina, L. T. and Molina, M. J.: Implementation of a Markov Chain Monte Carlo Method to inorganic aerosol modeling of observations from the MCMA-2003 Campaign. Part I: Model description and application to the La Merced Site, *Atmos. Chem. Phys.*, 6, 4867–4888, 2006a.
- San Martini, F. M., Dunlea, E. J., Volkamer, R., Onasch, T. B., Jayne, J. T., Canagaratna, M. R., Worsnop, D. R., Kolb, C. E., Shorter, J. H., Herndon, S. C., Zahniser, M. S., Salcedo, D., Dzepina, K., Jimenez, J. L., Ortega, J. M., Johnson, K. S., McRae, G. J., Molina, L. T., and

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Molina, M. J.: Implementation of a Markov Chain Monte Carlo Method to inorganic aerosol modeling of observations from the MCMA-2003 Campaign. Part II: Model application to the CENICA, Pedregal and Santa Ana sites, *Atmos. Chem. Phys.*, 6, 4889–4904, 2006b.

5 Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 161–180, 2003.

Sheehy, P. M., Volkamer, R. M., Molina, L. T., and Molina, M. J.: Radical Cycling in the Mexico City Metropolitan Area (MCMA): Modeling RO<sub>x</sub> Using a Detailed Mechanism, submitted, 2006.

10 Shivers, S.: Thermo Electron Corporation, Personal Communication, 2004.

Sickles, J. E., II; Nriagu, J. O., *Gaseous Pollutants: Characterization and Cycling*, John Wiley & Sons, Inc., 1992.

Smith, M. A. H., Rinsland, C. P., Fridovich, B., and Rao, K. N.: *Molecular Spectroscopy: Modern Research*, Academic Press, Inc., 1985.

15 Thornton, J. A., Wooldridge, P. J., and Cohen, R. C.: Atmospheric NO<sub>2</sub>: In Situ Laser-Induced Fluorescence Detection at Parts per Trillion Mixing Ratios, *Anal. Chem.*, 72, 528–539, 2000.

Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Williams, E. J., Hereid, D., Fehsenfeld, F. C., Stutz, J., and Alicke, B.: Comparisons of in situ and long path measurements of NO<sub>2</sub> in urban plumes, *J. Geophys. Res.*, 108, D16, 4496, doi:10.1029/2003JD003559, 2003.

20 Trainer, M., Buhr, M. P., Curran, C. M., Fehsenfeld, F. C., Hsie, E. Y., Liu, S. C., Norton, R. B., Parrish, D. D., Williams, E. J., Gandrud, B. W., Ridley, B. A., Shetter, J. D., Allwine, E. J., and Westberg, H. H.: Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, 96, D2, 3045–3063, 1991.

25 Velasco, E., Lamb, B., Westberg, H., Allwine, E., Sosa, G., Arriaga-Colina, J. L., Jobson, B. T., Alexander, M., Prazeller, P., Knighton, W. B., Rogers, T. M., Grutter, M., Herndon, S. C., Kolb, C. E., Zavala, M., Foy, B. d., Volkamer, R., Molina, L. T., and Molina, M. J.: Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 and 2003 field campaigns, *Atmos. Chem. Phys. Discuss.*, 6, 7563–7621, 2006.

30 Volkamer, R., Etzkorn, T., Geyer, A., and Platt, U.: Correction of the oxygen interference with UV spectroscopic (DOAS) measurements of monocyclic aromatic hydrocarbons in the atmosphere, *Atmos. Environ.*, 32, 3731–3747, 1998.

Volkamer, R., Molina, L. T., Molina, M. J., Shirley, T., and Brune, B.: DOAS measurement of

glyoxal as an indicator for fast VOC chemistry in urban air, *Geophys. Res. Lett.*, 32, L08806, doi:10.1029/2005GL022616, 2005.

Wesely, M. L. and Hicks, B. B.: A review of the current status of knowledge on dry deposition, *Atmos. Environ.*, 34, 2261–2282, 2000.

5 Williams, E. J., Baumann, K., Roberts, J. M., Bertman, S. B., Norton, R. B., Fehsenfeld, F. C., S.R. Springston, Nunnermacker, L. J., Newman, L., Olszyna, K., Meagher, J., Hartsell, B., Edgerton, E., Pearson, J. R. and Rodgers, M. O.: Intercomparison of ground-based  $\text{NO}_y$  measurement techniques, *J. Geophys. Res.*, 103, 22261–22280, 1998.

10 Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N.: Response of Commercial Comiluminouscent  $\text{NO-NO}_2$  Analyzers to Other Nitrogen-Containing Compounds, *Environ. Sci. Technol.*, 8, 13, 1118–1121, 1974.

ACPD

7, 569–604, 2007

---

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**Table 1.** Slopes of linear least squares fit of correlation plots of observed CL NO<sub>x</sub> monitor interference versus other measured species at series of locations. R<sup>2</sup> 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<sup>2</sup> 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<sub>2</sub>, O<sub>3</sub> and HNO<sub>3</sub> are highlighted as showing the best correlations.

Species Correlated with CL NO <sub>x</sub> Monitor Interference	ML STA	ML PED	ML MER	ML CEN	Roof CEN	Roof MER	Min	Max	Avg	R <sup>2</sup>
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 NH <sub>3</sub>	NA -0.03 (0.03)	NA 0.34 (0.04)	NA -0.06 (0.17)	-0.13 (0.04) 0.14	-0.15 (0.32) -0.05 (0.01)	NA 0.49 (0.01)	-0.15 -0.06	-0.13 0.49	-0.14 0.14	0.04–0.32 0.01–0.17
PAN AMS Particulate Nitrate	NA 2.44 (0.15)	NA 1.74 (0.12)	NA -0.44 (0.01)	ID 1.68 (0.01)	4.07 (0.09) 0.28 (0.01)	NA NA	-0.44	2.44	1.14	0.09 0.01–0.15
<b>NO<sub>2</sub></b>	<b>0.54 (0.65)</b>	<b>0.66 (0.79)</b>	<b>0.44 (0.32)</b>	<b>0.49 (0.35)</b>	<b>NA</b>	<b>NA</b>	<b>0.44</b>	<b>0.66</b>	<b>0.53</b>	<b>0.32–0.79</b>
<b>O<sub>3</sub></b>	<b>0.06 (0.30)</b>	<b>0.09 (0.54)</b>	<b>0.09 (0.19)</b>	<b>ID</b>	<b>0.11 (0.21)</b>	<b>0.15 (0.21)</b>	<b>0.06</b>	<b>0.19</b>	<b>0.10</b>	<b>0.19–0.54</b>
<b>HNO<sub>3</sub></b>	<b>NA</b>	<b>NA</b>	<b>NA</b>	<b>NA</b>	<b>1.83 (0.44)</b>				<b>1.83</b>	<b>0.44</b>

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**Table 2.** Averaged measured NO<sub>2</sub> concentrations for 5 week MCMA-2003 campaign by spectroscopic techniques compared to co-located CL NO<sub>x</sub> monitors at 4 locations.

Site	Spectroscopic Instrument	MCMA Campaign Average	CL NO <sub>x</sub> Monitor	MCMA Campaign Average	% Difference
La Merced	DOAS-UNAM	40.6	RAMA	49.5	+22%
CENICA	DOAS-1 DOAS-2	34.1 28.0	CENICA	31.0	-9% <sup>a</sup> ; +11%
Pedregal	TILDAS-ML <sup>b</sup>	27.6	ML <sup>b</sup> RAMA	29.4 30.7	+7% +11%
Santa Ana	TILDAS-ML <sup>b</sup>	3.8	ML <sup>b</sup>	9.1	140%

a = DOAS-1 believed to have larger NO<sub>x</sub> 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<sub>2</sub> concentration at each location.

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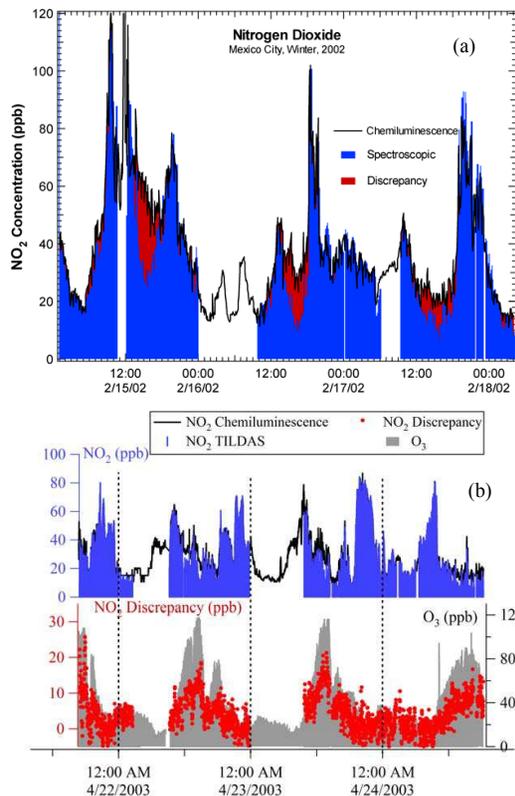
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## Evaluation of NO<sub>2</sub> Chemiluminescence Monitors

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**Fig. 1.** Panel (a) – Time series of NO<sub>2</sub> measurements by standard CL NO<sub>x</sub> 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<sub>x</sub> monitor interference is plotted on its own axis in this figure to show the correlation in time with ambient O<sub>3</sub> levels, which indicates a photochemical source of the interfering compound(s).

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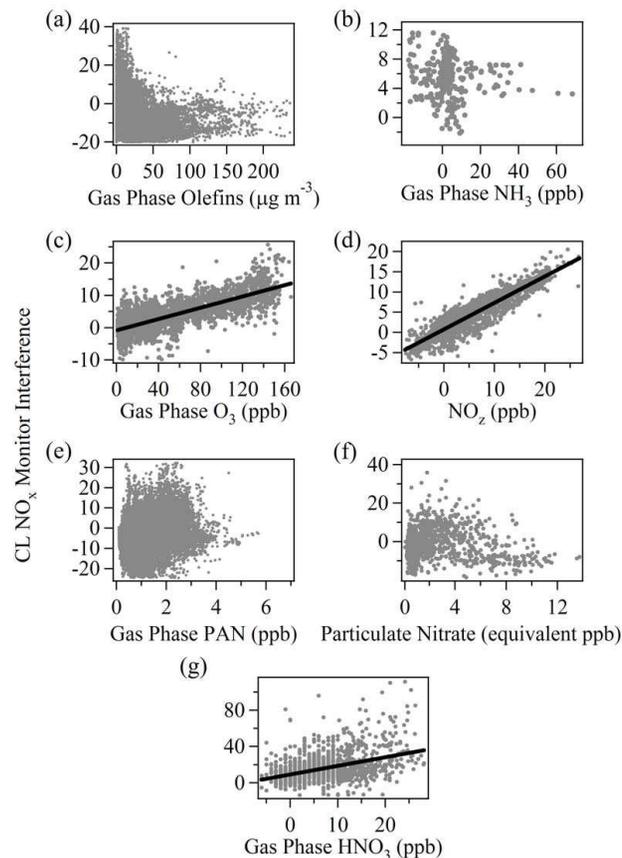
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**Fig. 2.** Linear regression plots for the CL NO<sub>x</sub> monitor interference plotted versus (a) gas phase olefins (CENICA), (b) gas phase NH<sub>3</sub> (Santa Ana), (c) gas phase O<sub>3</sub> (Pedregal), (d) NO<sub>2</sub> (Pedregal), (e) gas phase PAN (CENICA), (f) particulate nitrate (La Merced), and (g) gas phase HNO<sub>3</sub> (La Merced). See text for description of measurements. Results of the linear regressions are listed in Table 1.

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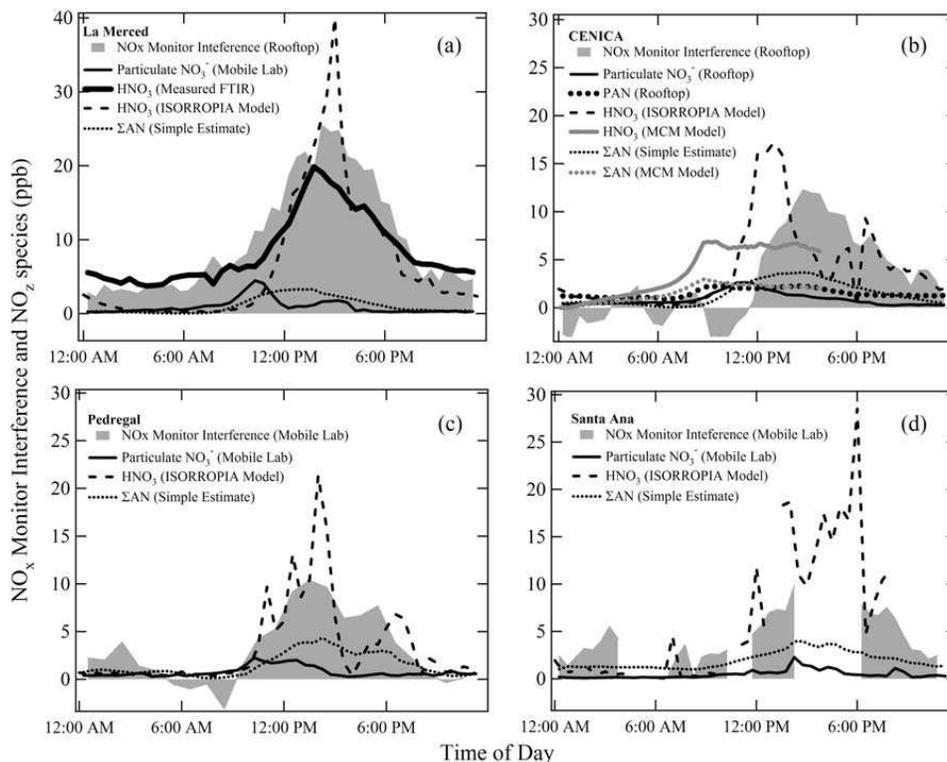
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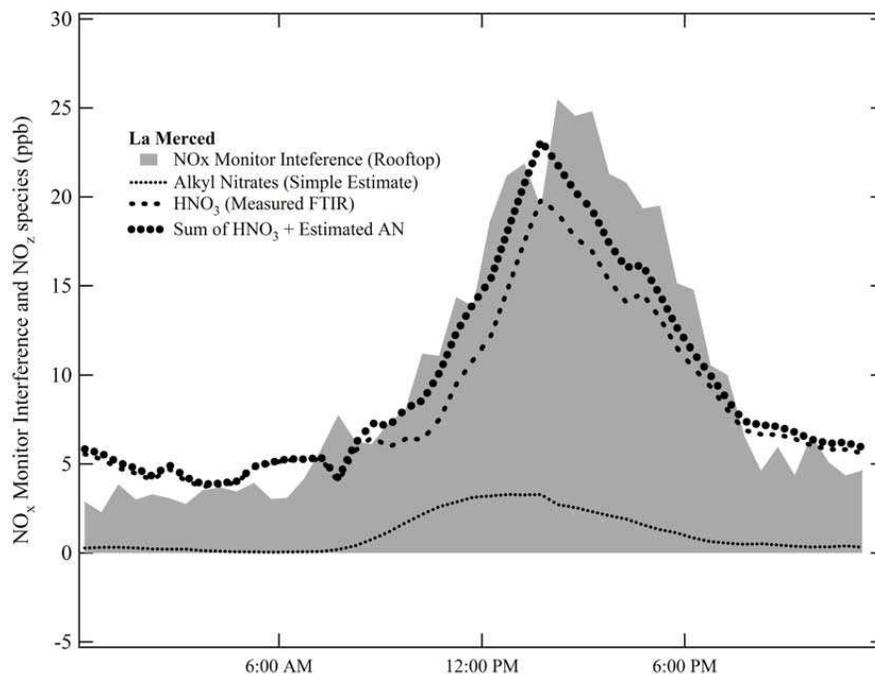
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**Fig. 3.** Diurnally averaged profiles for measured CL NO<sub>x</sub> monitor interference, calculated alkyl nitrate concentrations, measured PAN concentrations and measured particulate nitrate in equivalent gas phase concentration as observed at 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<sub>x</sub> monitor interference. Time of day is for local time. Gaps in profiles are due to limited data.

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**Fig. 4.** Diurnally averaged profiles for measured CL NO<sub>x</sub> monitor interference, measured HNO<sub>3</sub> concentrations and calculated alkyl nitrate concentrations at La Merced site. Also included is a profile of the sum of the measured HNO<sub>3</sub> concentration plus the estimated alkyl nitrate concentration (see text). Time of day is for local time.

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