Satellite observations of Mexico City pollution outflow from the Tropospheric Emissions Spectrometer (TES)

Changsub Shim, Qinbin Li, Ming Luo, Susan Kulawik, Helen Worden, John Worden, Annmarie Eldering, Glenn Diskin, Glen Sachse, Andy Weinheimer, David Knapp, Deedee Montzca, Teresa Campos

Jet Propulsion Laboratory, California Institute of Technology, CA, USA
Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA, USA
National Center for Atmospheric Research (NCAR), CO, USA
NASA Langley Research Center, VA, USA

Abstract
Concurrent tropospheric O3 and CO vertical profiles from the Tropospheric Emission Spectrometer (TES) during the MILAGRO/INTEX-B aircraft campaigns over the Mexico City Metropolitan Area (MCMA) and its surrounding regions were used to examine Mexico City pollution outflow on a regional scale. The pollution outflow from the MCMA occurred predominantly at 600–800 hPa as evident in O3, CO, and NOx enhancements in the in situ aircraft observations. TES O3 and CO are sensitive to the MCMA pollution outflow due to their relatively high sensitivities at 600–800 hPa. We examined O3, CO, and their correlation at 600–800 hPa from TES retrievals, aircraft measurements, and GEOS-Chem model results. TES captures much of the spatial and day-to-day variability of O3 seen in the in situ data. TES CO, however, shows much less spatial and day-to-day variability compared with the in situ observations. The $\Delta$O3/$\Delta$CO slope is significantly higher in the TES data (0.43) than the in situ data (0.28) due partly to the lack of variability in TES CO. Extraordinarily high $\Delta$O3/$\Delta$CO slope (0.81) from TES observations at 618 hPa over the Eastern U.S. was previously reported by Zhang et al. (Zhang, L., Jacob, D.J., Bowman, K.W., et al., 2006. Ozone–CO correlations determined by the TES satellite instrument in continental outflow regions. Geophys. Res. Lett. 33, L18804. 10.1029/2006GL026399.). Thus the application of TES CO–O3 correlation to map continental pollution outflow needs further examination.

1. Introduction
Mega-city pollution has been a major environmental concern in developing and developed countries alike (Fuchs et al., 1994). Pollution from these mega-cities has grave implications on regional to global air quality and climate change (Mage et al., 1996; Molina and Molina, 2004). One of the world’s most densely populated mega-cities, the Mexico City Metropolitan Area (MCMA: ∼ 19°N, ∼ 99°W, ∼ 750 hPa), with a population of over 19 million within an area of ∼ 1500 km², is among the most polluted cities (IPCC, 2007). Large emissions of air pollutants from the MCMA result from pervasive incomplete combustion including low-temperature household cooking and heating and from vehicle emissions (CAM, 2001). In 1998, for example, the total volatile organic compounds (VOCs) emissions from the MCMA (475 Gg/yr) is higher than that from Los Angeles (362 Gg/yr in 2001), the most polluted mega-city in the United States (Molina and Molina, 2002). The MCMA is located in the Valley of Mexico, a large basin in the high plateaus at the center of Mexico, at an altitude of 2.2 km above sea level, surrounded by mountains on all four sides except a small opening at the north. The basin is often under the influence of high pressure systems, whose weak winds and persistent boundary layer thermal inversions often trap pollution to within the basin (Molina and Molina, 2002).

The MILAGRO/INTEX-B aircraft campaigns in March 2006 aimed to investigate the emissions, transport, and physiochemical transformation of key air pollutants from the MCMA (www.joss.ucar.edu/milagro/; Singh et al., submitted). During this campaign, the synoptic scale export of the MCMA pollution out of the Valley of Mexico is generally controlled by thermal-driven circulations in the...
boundary layer and southwesterly wind in the middle troposphere (Fast et al., 2007). Airborne measurements of various gaseous and aerosol pollutants were made aboard the NASA DC-8 and NSF C-130 aircrafts. In coordination with the aircraft observations, the Tropospheric Emission Spectrometer (TES) instrument aboard the Aura satellite conducted several special observations and global surveys (see Section 2.2) during the campaigns. TES provides concurrent global three-dimensional (3-D) mapping of tropospheric O₃ and CO (Beer, 2006).

Some recent studies have explored the use of space-borne observations to examine regional to global air pollution (Boersma et al., 2008; Clerbaux et al., 2008; Massie et al., 2006; Zhang et al., 2008). For example, Zhang et al. (2006) has shown that TES tropospheric data can be used to map global pollution and continental outflow. They found positive O₃–CO correlations and slopes of tropospheric data can be used to map global pollution and continental outflow (Beer, 2006). We use here O₃ and CO data from all eight Step and Stares and four global surveys from March 2006. The corresponding TES orbital tracks over the MCMA region during MILAGRO/INTEX-B are shown in Fig. 1 (right panel).

2. Methodology

2.1. Aircraft measurements

A suite of chemical tracers including O₃, CO, NOₓ, and VOCs were measured aboard the C-130 and DC-8 during the MILAGRO/INTEX-B campaigns. Fig. 1 (left panel) shows the aircraft flight tracks. The C-130 flights stayed closer to the MCMA compared with those of the DC-8 with the later covering a much larger domain. O₃ and CO were measured by Chemiluminescence Detector (CLD) and Tunable Diode Laser (TDL), respectively (Avery et al., 2001; Madronich et al., 2004; Sachse et al., 1987) on the both C-130 and DC-8. The precisions of O₃ and CO are 3–7% and 1%, respectively with ±5% accuracy (Richards et al., 2008; Sachse et al., 1987; Singh et al., submitted). We used the 1-minute merged data. Our analysis focuses on observations from March 4–31, 2006 within 15°N–25°N and 95°W–103°W (rectangle, Fig. 1).

2.2. TES data

TES measures infrared emissions with high spectral resolution (0.1 cm⁻¹) and a wide spectral range from 660 to 2260 cm⁻¹ (Beer et al., 2001). TES overpass times (ascending node) are 01:45 and 13:45 local time. TES has a footprint of ~5 × 8 km nadir, about 180 km apart between consecutive measurements along the orbital tracks in the standard Global Survey mode. Global coverage is achieved in 16 days. In the Step and Stare special observation mode, TES provides denser nadir spatial coverage (~40 km apart between consecutive measurements along the orbit) over a 60° latitudinal range (Beer, 2006). We use here O₃ and CO data from all eight Step and Stares and four global surveys from March 2006. The corresponding TES orbital tracks over the MCMA region during MILAGRO/INTEX-B are shown in Fig. 1 (right panel).

TES retrievals of O₃ and CO are based on the optimization between modeled a priori and observed radiance with maximum a posteriori method (Rogers, 2000) and the details of the retrieval algorithms are described in Worden et al. (2004), Bowman et al. (2002, 2006), and Luo et al. (2007a). Here we use the version 3 data (V003, F04_04) (Osterman et al., 2006) available at the time of this study. The degrees of freedom for signal (DOFs) for O₃ and CO are 1.6 and 1.4, respectively in the troposphere (Worden et al., 2004; Bowman et al., 2006; Luo et al., 2007b). TES sensitivity is reduced by ~40% with a cloud optical depth of 0.1 in the lower troposphere (Kulawik et al., 2006). We excluded TES retrievals when cloud optical depth is larger than 0.2.

The validation of TES data with in situ measurements requires applying TES averaging kernels to in situ profiles to take into account the relatively coarse TES vertical resolution and a priori information (Rodgers and Connor, 2003; Worden et al., 2007). On average, TES O₃ shows a positive bias of ~6 ppbv (15%) throughout the troposphere in comparison with ozonesonde data (Nassar et al.,...
Richards et al. (2008) compared TES O₃ data with airborne in situ measurements during INTEX-B and found a positive bias of ~2–6 ppbv (5–15%) in the troposphere. TES CO has been validated with aircraft data during the Aura Validation Experiments (AVEs) by Lopez et al. (2008). They found that TES CO is slightly lower than the in situ data (~10% or ~8 ppbv) in the middle latitudes and slightly higher (5–10% or ~4–8 ppbv) in the tropics. Luo et al. (2007b) conducted TES CO validations during INTEX-B and showed consistent results (a negative bias of <10%). Due to the lack of concurrent TES and in situ measurements, relaxed coincident criteria such as within ~600 km distance and ~48 h were used in the aforementioned validations.

Fig. 2 shows the closest TES orbital track (a Global Survey) to the MCMA on March 19th, 2006 (left panel) and averaging kernels for O₃ and CO (upper and lower right panels) along the orbital track between 15°N and 25°N over Mexico. The closest distance between the MCMA and this TES orbital track is 95 km at location “a” (Fig. 2) over the Mexico City Basin (~20°N, ~750 hPa) where there is relatively poor sensitivity for both O₃ and CO. The reason for the weak sensitivity is under further investigation by the TES retrieval team (K. Bowman, personal communication, 2008, Jet Propulsion Laboratory). By contrast, O₃ and CO averaging kernels away from the Mexico City Basin (~23.3°N, ~850 hPa; location “b” in Fig. 2) show largest sensitivities to 600–800 hPa, typical for the middle and low troposphere under clear sky (e.g., Jones et al., 2003; Luo et al., 2007a; Richards et al., 2008; Worden et al., 2007; Zhang et al., 2006).

To illustrate the latitudinal variations of TES O₃ and CO averaging kernels, the diagonals of the TES O₃ and CO averaging kernels from the March 12th TES Step and Stares are shown in Fig. 3 for 5°–35°N. The closest distance from the orbital track to the MCMA is ~150 km. While there is relatively large sensitivity in the lower to middle troposphere, there is poor sensitivity for both O₃ and CO over the Mexico City Basin (17°N–20°N). Thus it appears that TES data are sensitive to the MCMA pollution outflow, rather than the pollution right over Mexico City Basin itself.

2.3. GEOS-Chem

GEOS-Chem is a global 3-D chemical transport model driven by assimilated meteorological data from NASA Global Modeling Assimilation Office (GMAO) (Bey et al., 2001). We use version 7-04-10 (http://www.as.harvard.edu/chemistry/trop/geos) of the model, driven by GEOS-4 meteorological data with a horizontal resolution of 2° × 2.5° and 30 vertical layers. The meteorological fields are updated every six hours, and the surface fields and mixing depths are updated every three hours.

GEOS-Chem includes a comprehensive tropospheric O₃–NOₓ–VOC chemistry mechanism. Climatological monthly mean biomass burning emissions are from Duncan et al. (2003). The fossil fuel emissions are from the Emission Database for Global Atmospheric Research (EDGAR) inventory for NOₓ, CO, and SO₂ and from the Global Emission Inventory Activity (GEIA) for other chemical compounds (Benkovitz et al., 1996; Olivier and Berdowski, 2001). These emissions are updated with particular national emission inventories and fuel use data: the Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) inventory for Mexico (Kuhns et al., 2005) and U.S. EPA NEI 99 inventory (National Emissions Inventory, base year 1999, version 3) for the continental U.S. (EPA, 2004). The biogenic VOCs emissions are based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN) inventory (Guenther et al., 2006). The lightning NOₓ emissions are parameterized based on cloud top height and regionally scaled to climatological satellite observations of flash rates (Hudman et al., 2007). We conducted GEOS-Chem simulations for September 2005–March 2006 with the first six months for initialization. We focus our analysis on March 2006. Model results are sampled along the aircraft flight tracks and TES orbital tracks.

To compare GEOS-Chem results with TES retrievals, model profiles of O₃ and CO are convoluted with TES averaging kernels to account for the different sensitivities and a priori information of TES retrievals to different pressure levels (Jones et al., 2003; Richards et al., 2008). The resulting model profiles can then be directly compared with TES retrievals (Zhang et al., 2006; Jourdain et al., 2007; Worden et al., 2007).

We note here that the emissions used in our GEOS-Chem simulations are not 2006-specific. Additionally, the horizontal resolution of 2° × 2.5° may be too coarse for resolving details of the regional pollution outflow. GEOS-Chem simulations with 1° × 1° nested simulations over North America have been done before (e.g., Li et al., 2005) but not available for 2006 at the time of this study.
We include GEOS-Chem results for comparison despite the aforementioned shortcomings in our model simulations. Improving model simulations for the MILAGRO/INTEX-B period is obviously required to understand the processes controlling the MCMA outflow. It is however beyond the scope of the present analysis.

3. Results and discussions

3.1. Mexico City pollution outflow

The median vertical profiles of O₃, CO, and NOₓ mixing ratios from the aircraft measurements during MILAGRO/INTEX-B are shown separately for DC-8 and C-130 in Fig. 4. Data points below the 800 hPa pressure level were from observations at lower altitudes further away from the high-elevation MCMA. Values shown in Fig. 4 are binned every 50 hPa vertically. The NOₓ profiles are shown here in addition to O₃ and CO for the purpose of indicating the altitude range for the MCMA pollution outflow. The outflow occurs mainly at 600–800 hPa, corresponding to the high elevation of the Mexico City Basin (≈750 hPa), as indicated by the enhanced O₃, CO, and NOₓ levels.

There are generally higher concentrations for all three pollutants, O₃, CO, and NOₓ at 500–800 hPa in the C-130 observations than those from the DC-8, while the later shows higher concentrations at 700–900 hPa. The higher concentrations in the C-130 observations at 500–800 hPa are due presumably to the proximity of the C-130 flights to the urban area of the MCMA (Fig. 1) thus exposure to more pollution events. The higher concentrations in the DC-8 observations at 700–900 hPa likely indicate the export of the MCMA pollution by the prevailing southwesterlies in the middle troposphere to downwind regions (e.g., near the Gulf of Mexico) where there is more DC-8 coverage, followed by subsidence (Fast et al., 2007).

As stated in the Section 2.2, TES averaging kernels were applied to in situ profiles for direct comparisons in previous TES validation studies with relaxed coincidence criteria. However, such coincidence criteria are generally inappropriate for a relatively small regional domain such as the one used in the present analysis (rectangle, Fig. 1). During MILAGRO/INTEX-B there is only one coincident spiral profiling by the DC-8 for TES validation on March 12th (23°N and 98.5°W, ≈450 km away from the MCMA). Validation results using the profiles from that spiral have been reported by Richards et al. (2008) and Luo et al. (2007b) and those were cited in Section 2.2. In general, direct comparisons of absolute mixing ratios between TES and in situ data over the MCMA and its surrounding regions can be challenging primarily because of the scarcity of coincident TES and aircraft profiles. We instead intend to investigate the spatial and temporal variabilities of O₃ and CO and the O₃–CO correlation as seen from TES and in situ data and GEOS-Chem results.
3.2. Vertical distributions of TES tropospheric O3 and CO over the MCMA

Fig. 5 shows individual TES vertical O3 profile during MILAGRO/INTEX-B (gray dots) within the domain defined in Fig. 1. The median TES vertical O3 profile is also shown (data binned every 50 hPa). We focus our analysis on the 600–800 hPa pressure levels where most of the MCMA outflow occurs (Fig. 4). Large enhancements and variations in O3 are seen in several profiles. Such enhancements are not seen in the TES a priori (not shown). In addition, the mean DOFs is greater than 0.4 at 600–900 hPa, indicating that the TES O3 profiles are not entirely determined by the a priori. Fig. 6 shows the corresponding individual and monthly median vertical profiles of TES CO. Several profiles with enhanced CO concentrations at 500–800 hPa (>130 ppbv) are not seen in the a priori (not shown).

Also shown in Figs. 5 and 6, TES O3 and CO profiles over unpolluted regions over the tropical Pacific adjacent to the west coast of Mexico (103°W–107°W, 15°N–25°N, black dots in Figs. 5 and 6). The notably enhanced concentrations (>70 ppbv for O3 and >130 ppbv for CO, indicated by the gray dots) are only seen in the profiles over the MCMA and its downwind regions. This indicates that TES captures the enhancements of O3 and CO on a regional scale as a result of the MCMA pollution outflow.

Fig. 7 shows the zonal mean of TES O3 and CO in March 2006 over the domain defined in Fig. 1 (rectangle). TES does not clearly show the pollution over the Mexico City Basin (~19°N) due mainly to the retrieval issues (see Section 2.2). The enhanced TES O3 and CO between 20°N and 23°N is likely due in part to the MCMA pollution outflow transported by the southwesterly. This pattern is seen in TES data from other years (not shown).

3.3. O3 and CO variabilities over the MCMA

Our analysis in this Section focuses on the variabilities of lower tropospheric O3 and CO and to what degree they are captured by TES observations. More specifically, we examine the day-to-day and spatial variabilities of TES O3 and CO in comparison with the in situ observations. Fig. 8 shows time series of O3 and CO from the in situ aircraft observations and TES retrievals during MILAGRO/INTEX-B. Values shown are for 600–800 hPa. The in situ data are shown without applying TES averaging kernels for reasons discussed in Section 3.1. GEOS-chem model results are also shown without TES averaging kernels applied. On average the application of TES averaging kernels to GEOS-Chem concentration fields makes little difference: <1 ppbv for O3 and <6 ppbv for CO, respectively. We emphasize here that Fig. 8 is intended for examining spatial and temporal varibilities of O3 and CO instead of their absolute magnitudes among the three data sets.

The in situ data in Fig. 8 indicate nine strong pollution days: March 4th, 8th, 10th, 11th, 12th, 16th, 19th, 22nd, and 29th with O3
are indicative of the spatial variabilities of O\textsubscript{3} and CO during the course of the observations. An example is shown in Fig. 1. This would conceivably contribute to higher $\Delta O_{3}/\Delta CO$ enhancement ratios. We examine in this section the $O_{3}$–$CO$ correlations and slopes for 600–800 hPa derived from the aircraft measurements, TES retrievals, and GEOS-Chem results during MILAGRO/INTEX-B. The results are summarized in Table 1 and shown in Fig. 10. All the data are averages on $2^{\circ} \times 2.5^{\circ}$ grids over the domain defined in Fig. 1.

The in situ aircraft observations during MILAGRO/INTEX-B show a strong $O_{3}$–$CO$ correlation (correlation coefficient $R = 0.78$) and a positive $\Delta O_{3}/\Delta CO$ enhancement ratio of 0.28 mol mol$^{-1}$ for the domain defined in Fig. 1. The regression results were derived using the reduced major axis method (Hirsch and Gilroy, 1984). The slope is within the range of those derived from summertime in situ measurements over the Eastern U.S. at the surface and in the lower troposphere: $\Delta O_{3}/\Delta CO = 0.2$–0.4 mol mol$^{-1}$ with $R = 0.7$–0.9 (e.g., Chin et al., 1994; Parrish et al., 1993). In comparison, slopes derived from the International Consortium on Atmospheric Transport and Transformation (ICARTT) aircraft campaigns in July–August 2004 (Fehsenfeld et al., 2006; Singh et al., 2006) are $\Delta O_{3}/\Delta CO = 0.31$–0.44 mol mol$^{-1}$ with $R = 0.5$–0.67 in the lower troposphere over the Eastern U.S. ($30^\circ$ N–$50^\circ$ N, $50^\circ$ W–$100^\circ$ W, and surface-600 hPa). Previously, Zhang et al. (2006) reported a slope of $\Delta O_{3}/\Delta CO = 0.72$ mol mol$^{-1}$ derived from in situ aircraft measurements during the same ICARTT campaign over the Eastern U.S. The difference is that Zhang et al. (2006) excluded fresh pollution plumes (NO$_x$/NO$_y > 0.4$ mol mol$^{-1}$, altitude < 3 km, and HCN > 500 pptv or CH$_3$CN > 225 pptv) and stratospheric influence ($O_{3}/CO > 1.25$ mol mol$^{-1}$) within a smaller domain ($30^\circ$ N–$40^\circ$ N, $70^\circ$ W–$80^\circ$ W, and 600–650 hPa). In comparison, following Zhang et al. (2006) except without excluding fresh pollution and stratospheric influence, the $\Delta O_{3}/\Delta CO$ for the ICARTT campaigns is 0.55 mol mol$^{-1}$, significantly lower than that reported by Zhang et al. (2006).
Table 1

<table>
<thead>
<tr>
<th>Location</th>
<th>Time period</th>
<th>Pressure</th>
<th>( r )</th>
<th>( \Delta \text{O}_3/\Delta \text{CO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCMA in situ</td>
<td>March 2006</td>
<td>600–800 hPa</td>
<td>0.78 (0.69)</td>
<td>0.28 ± 0.07</td>
</tr>
<tr>
<td>TES</td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.43 ± 0.1</td>
</tr>
<tr>
<td>GC/AK ( ^c )</td>
<td></td>
<td></td>
<td>0.58</td>
<td>0.25 ± 0.06</td>
</tr>
<tr>
<td>GC-raw ( ^d )</td>
<td></td>
<td></td>
<td>0.26</td>
<td>0.3 ± 0.15</td>
</tr>
<tr>
<td>Eastern U.S. ( ^e )</td>
<td>1991–1994</td>
<td>Surface</td>
<td>0.53</td>
<td>0.81 Zhang et al. (2006)</td>
</tr>
<tr>
<td></td>
<td>July 2005</td>
<td>618 hPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Western Pacifc</td>
<td>February–March, 2001</td>
<td>Surface</td>
<td>0.5–0.7</td>
<td>0.31 – 0.44 ICARTT</td>
</tr>
<tr>
<td>Eastern U.S.</td>
<td>June–August, 1988–1991</td>
<td>Surface</td>
<td>0.7–0.9</td>
<td>0.15 TRACE-P Chin et al. (1994)</td>
</tr>
<tr>
<td>Sable Island</td>
<td>July–September, 1991</td>
<td>Surface</td>
<td>0.82</td>
<td>~0.3 Parrish et al. (1993)</td>
</tr>
</tbody>
</table>

The data for this study were averaged onto \( 2^\circ \times 2.5^\circ \) grids over the MCMA (rectangle, Fig. 1).

\( ^a \) The correlation coefficient inside parenthesis indicates the result excluding the fresh pollution plumes and stratospheric \( \text{O}_3 \) influence according to Zhang et al. (2006) and Hudman et al. (2007).

\( ^b \) The \( \Delta \text{O}_3/\Delta \text{CO} \) derived from the same data as \( a \).

\( ^c \) GEOS-Chem results with TES averaging kernels applied.

\( ^d \) GEOS-Chem results without applying TES averaging kernels.

\( ^e \) TES version 1 (V001) data.

\( ^f \) The data were selected from DC-8 between 30° N–50° N and 50° W–100° W without the filtering as \( a \).
observations. There is significantly smaller spatiotemporal variability in addition to a low bias in TES lower tropospheric CO compared with in situ observations over the MCMA and its surrounding regions. Both likely contribute to the apparent overestimate of TES $\text{O}_3$/$\text{CO}$ enhancement ratios during MILAGRO/INTEX-B (0.43 mol mol$^{-1}$) compared with that from the in situ data (0.28 mol mol$^{-1}$). Thus, the use of TES tropospheric O$_3$ and CO retrievals for mapping continental pollution outflow needs further examination.

Acknowledgements

This work was performed at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under contract with the NASA. C. Shim and Q. Li were jointly supported by the JPL Research and Technology Development (R&T) program, Human Resources Development Fund (HRDF), NASA Atmospheric Composition Modeling and Analysis program (ACMAP), and the TES project at JPL. The GEOS-Chem model is managed at Harvard University with support from the NASA Atmospheric Chemistry Modeling and Analysis Program. We thank Melody Avery for the in-situ O$_3$ measurements. We thank Lin Zhang for very helpful discussions.

References


