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Tula industrial complex (Mexico) emissions of SO_2 and NO_2 during the MCMA 2006 field campaign using a mobile mini-DOAS system

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Abstract. The Mexico City Metropolitan Area (MCMA) has presented severe pollution problems for many years. There are several point and mobile emission sources inside and outside the MCMA which are known to affect air quality in the area. In particular, speculation has risen as to whether the Tula industrial complex, located 60 km northwest of the MCMA has any influence on high SO_2 levels occurring on the northern part of the city, in the winter season mainly. As part of the MILAGRO Field Campaign, from 24 March to 17 April 2006, the differential vertical columns of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) were measured during plume transects in the neighborhood of the Tula industrial complex using mobile mini-DOAS instruments. Vertical profiles of wind speed and direction obtained from pilot balloons and radiosondes were used to calculate SO_2 and NO_2 emissions. According to our measurements, calculated average emissions of SO_2 and NO_2 during the field campaign were 384 ± 103 and 24 ± 7 tons day^{-1}, respectively. The standard deviation of these estimations is due to actual variations in the observed emissions from the refinery and power plant, as well as to the uncertainty in the wind fields at the exact time of the measurements. Reported values in recent inventories were found to be in good agreement with calculated emissions during the field campaign. Our measurements were also found to be in good agreement with simulated plumes.

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1 Introduction

The Tula industrial complex is located northwest of the Mexico City Metropolitan Area (MCMA), in the State of Hidalgo, Mexico. It is close to a number of other industries in the Tula-Vito-Apasco industrial corridor (Fig. 1). According to the latest information from the federal environmental authority 323 ktons per year (ktpy) of SO_2 and 44 ktpy of NO_x are released in this region. The main emitters are the Miguel Hidalgo Refinery (MHR) and the Francisco Pérez Ríos Power Plant (FPRPP) (SEMARNAT, 2002). Other industries such as cement plants, open-sky mines and agricultural activities are also responsible of important particle matter emissions into the atmosphere and for soil degradation of the area. The MHR processes 296 thousand barrels per day (TBD) of crude oil, representing 20% of the total refining capacity in the country. Final products are mainly gasoline, diesel, turbosine, kerosene, and other subproducts used to improve fuel specifications. To satisfy internal energy demand, the refinery consumes gas and liquid residuals of the refining processes, often of poor quality (3.8% weight of sulfur content). The FPRPP has an installed capacity of 2000 megawatt (MW), distributed in 9 units combining vapor (five) and combined cycle (four) technologies. These two industries contribute almost 90% of SO_2 and 80% of NO_x of the total emission in Hidalgo State (IMP, 2006).

NO_2 is of special interest due to its potential for undergoing photochemical reactions and producing, together with volatile organic compounds; ozone, peroxyacetyl nitrate, nitric acid, formaldehyde and formic acid, among others (Finlayson-Pitts and Pitts, 2000). Long term exposure of humans to NO_2 has negative health effects such as lung

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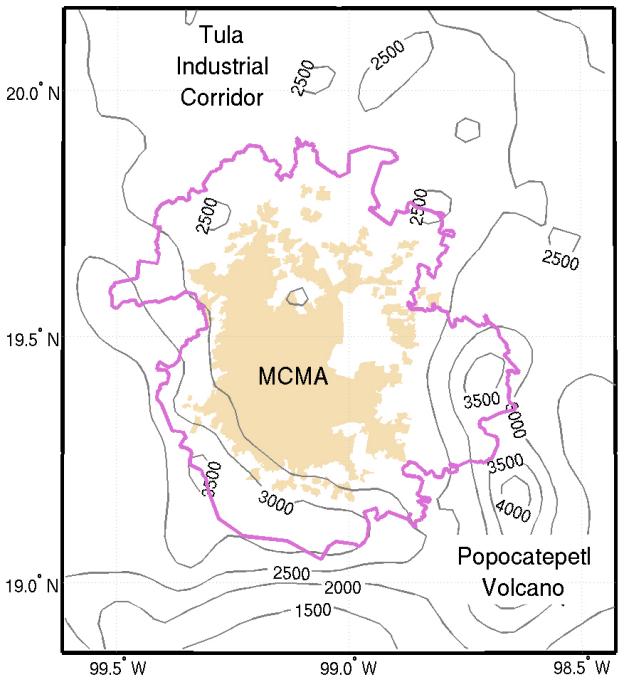

Fig. 1. Location of the Tula industrial corridor, urban area of the MCMA in beige. Terrain contours every 500 m.

function decrease and higher risk of respiratory symptoms. SO_2 was shown to lead to reductions in FEV1 (Forced Expiratory Volume in 1 s) and other indices of ventilatory capacity, as well as to increased mortality and hospital emergency admissions for total respiratory cases and chronic obstructive pulmonary disease at lower levels of exposure (WHO, 2000). In addition to their negative effects on human health, SO_2 and NO_2 tend to form sulfuric and nitric acids respectively, which through dry and wet deposition contribute to damage of plants and buildings.

Because of its large emissions, the Tula industrial complex is thought to affect air quality in the MCMA. Since the early 2000's, the atmospheric monitoring network of the MCMA, has been reporting unusual high SO_2 concentrations during night time at the northern part of the MCMA. According to a 2003 report of the "Program to Improve Air Quality in Mexico City Metropolitan Area 2002–2010" (CAM, 2003) in some occasions SO_2 concentrations in the north part of the city have exceeded the Mexican Air Quality Standard (0.13 ppm 24 h-average). It has not been possible to attribute this to irregular operations of industries located in the surrounding area. For this reason, it has been questioned whether the Tula industrial zone is responsible for worsening air quality in the MCMA. Mexican Petroleum (PEMEX) and Federal Commission of Electricity (CFE) companies located at the Tula industrial complex, however, claim to comply with emission regulations, and therefore not to affect air quality.

De Foy et al. (2007) used Concentration Field Analysis using backward trajectories during the MCMA-2003 field campaign to identify possible source regions of SO_2. These were found to be to the northwest of the MCMA, in the direction of the Tula industrial zone. Forward modeling using measured emissions from the complex showed that these could account for the large SO_2 peaks observed in the MCMA, but that they only contribute 20% of the long term average concentration. Local sources are the dominant cause of baseline SO_2 levels. The Popocatépetl volcano is another large point source that affects the MCMA and leads to increased sulfate aerosol production in the city (Raga et al., 1999) even though impacts during MCMA-2003 were shown to be possible but could not be differentiated from the local levels (de Foy et al., 2007).

To address the issue of emissions from the refinery and the power plant, the total fluxes of SO_2 and NO_2 were determined by measurements of their respective integrated vertical columns in the neighborhood of the Tula industrial zone. The importance of this study relies on the possibility to verify published emission inventories and provide detailed emission information for modeling studies.

2 Methods

2.1 Mobile mini-DOAS

SO_2 and NO_2 emissions have been determined using Differential Optical Absorption Spectroscopy (DOAS). DOAS is a spectroscopic technique based on the absorption of electromagnetic radiation by matter, allowing the remote detection of trace gases. DOAS instruments have been developed in a wide variety of designs and measurements can be performed using several experimental setups (Platt and Stutz, 2008).

In this field campaign, scattered UV sunlight in the zenith position was collected by mobile mini-DOAS instruments installed on a car, while traversing underneath the plumes of the industrial sites. SO_2 and NO_2 emissions were determined by integrating the total number of molecules in a vertical cross-section of the gas plume, and multiplying them by the wind speed at plume height. The instrument is referred to as mini-DOAS due to its small size and low weight. The mobile mini-DOAS collects scattered ultraviolet sunlight using a telescope equipped with a quartz lens; the light enters a spectrometer through an optical fiber (Galle et al., 2002). The spectrometers used in this study have a spectral resolution of about 0.6 nanometers (nm) and spectral range of 280–420 nm for SO_2 and 336–480 nm for NO_2. Similar equipments have been successfully used to quantify SO_2 emissions from volcanoes (Bobrowski et al., 2003; Edmonds et al., 2003; Galle et al., 2002; McGonigle et al., 2002; Mori et al., 2006; O'Dwyer et al., 2003), industries (McGonigle et al., 2004; Rivera et al., 2009) and urban areas (Johansson et al., 2008, 2009).

A general spectral evaluation procedure was applied to every spectrum collected during a traverse, starting with dark current correction of every recorded spectrum, division with a "clean-air" reference spectrum, the application of a high pass filter to separate broad and narrow band spectral structures and finally a logarithm of the spectrum. For each traverse, the "clean-air" reference spectrum has been selected as the first spectrum in the measurement, as this reduces the time difference between the collection of the "clean-air" reference and each of the subsequently measured spectra. As already pointed out by Sinreich et al. (2005), this procedure can help to eliminate the contribution of stratospheric NO_2 to the signal and give less influence of instrumental instabilities. Afterwards a non-linear fitting of several absorption cross sections is made to the measured spectra, obtaining vertical columns of the gases of interest which are differential with respect to the vertical columns in the "clean-air" reference spectrum. The fitting intervals used correspond to 307–317 nm and 415–455 nm for SO_2 (Bogumil et al., 2003) and NO_2 (Vandaele et al., 1998) cross sections, respectively. The O_3 cross section (Voigt et al., 2001) was included in the fitting procedure for both SO_2 and NO_2 as well.

The mobile mini-DOAS instrument was complemented with a Global Positioning System (GPS), both of them connected to a laptop computer and controlled by custom-built software -MobileDOAS- (Johansson and Zhang, 2004) which collects and evaluates acquired spectra in real time. The mobile mini-DOAS instrument was mounted on a car and spectra were recorded, at different distances from the source, both encircling the source and traversing downwind the pollutants plume. For each collected spectrum, GPS data was recorded providing time and position before and after the spectrum was collected.

Fluxes from traverses were calculated multiplying differential vertical columns by the distance traversed perpendicular to the wind direction, and by the wind speed at plume height. The corresponding methods for obtaining meteorological information are discussed in the following section.

2.2 Meteorological measurements

For accurately quantifying emissions, the mobile mini-DOAS technique requires wind speed and wind direction information at the height of the plume. Therefore, these parameters were measured at surface and aloft, using different methods. The meteorological equipment was deployed at a Mexican Petroleum Institute (IMP) site (Longitude 99°16′ 24.4″ W and Latitude 20°2′ 48.6″ N), located inside the MHR facilities. A surface meteorological station (MAUS-210 from Vaisala) registered continuously those variables 10 m above the ground, while vertical measurements were performed using pilot balloons and radiosondes.

Wind data from pilot balloons were used to calculate SO_2 and NO_2 emissions for measurements performed between 24 and 26 March 2006 because they were more frequently launched than radiosondes. For measurements performed after 27 March 2006, results from radiosondes were used instead, being our only source of wind data available at plume height.

2.2.1 Pilot balloons

Pilot balloons were launched during 24–26 March 2006 with a frequency of 1–2 h during daytime, in order to obtain information on the vertical distribution of wind speed and direction at plume height. The pilot balloons were filled with a pre-determined amount of commercial helium, resulting in a standardized uplift force. The ascent rate was estimated by intercomparisons with radiosonde data (see Fig. 2). Once the balloons were launched, they were tracked by theodolites (Tamaya model TD3), and both azimuth and elevation were registered in 10 s intervals. The position of the balloon in space was calculated from these angles from which wind speed and direction were derived.

2.2.2 Radiosondes

A Digicora II radiosonde system from Vaisala (Mod. SPS-220) was used for upper air sounding measurements of pressure, temperature, relative humidity and the horizontal wind vector. The radiosonde system consists of a ground-base station that receives and stores the incoming signal from the radiosonde transmitter; a radiosonde that supports all meteorological sensors, and a meteorological balloon that raises the sonde from the ground to the upper atmosphere. The radiosondes were launched four times a day from 16 March to 22 April 2006 at 08:00, 12:00, 15:00 and 18:00 h (local time) by using 300 g latex-helium-filled balloons.

2.3 Modeling

Forward plume simulations were carried out using Lagrangian particle trajectories. The mesoscale meteorology was simulated with the Weather Research and Forecast (WRF) model version 3.0.1 (Skamarock et al., 2005). Three nested grids were used with resolutions of 27, 9 and 3 km, and wind fields were saved every hour. The simulation options and model evaluations are described in de Foy et al. (2009). Stochastic particle trajectories were calculated with WRF-FLEXPART (Doran et al., 2008; Stohl et al., 2005). 1800 particles per hour were released from a single stack representing FPRPP and 720 particles per hour from a stack representing MHR. Plume rise was calculated using the algorithm in CAMx (ENVIRON, 2009) on an hourly basis. This yielded particle release heights varying from 175 to 1400 m AGL for FPRPP and from 75 to 1000 m AGL for MHR, depending on the time of day and on stability conditions.

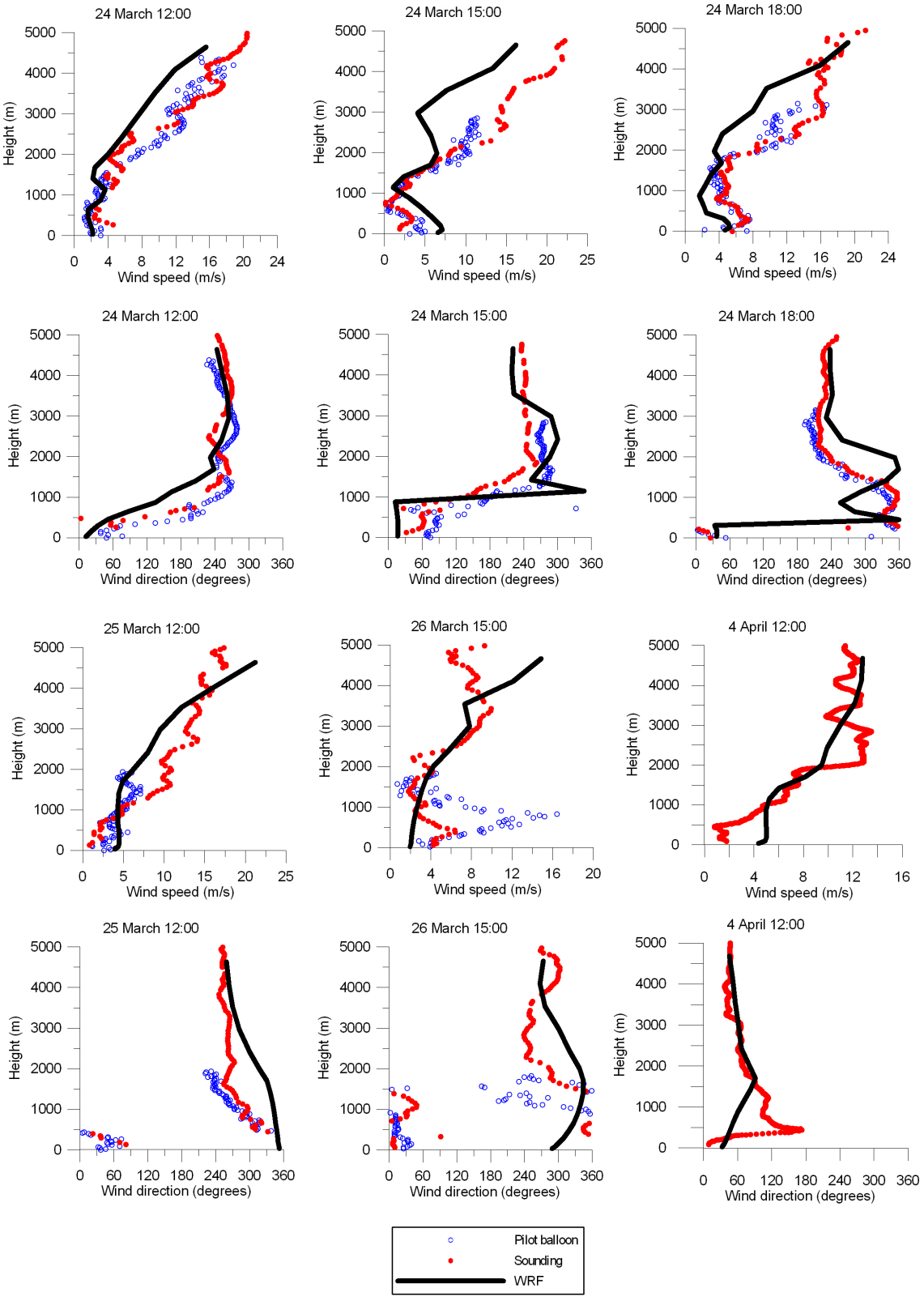

Fig. 2. Wind speed and wind direction comparison between pilot balloon, sounding and WRF for 24, 25 and 26 March 2006. Comparisons are presented only when coincident information of the three methods is available. Additionally wind speed and wind direction results from a sounding launched on 4 April 2006 at 12:00 local time are presented together with WRF results.

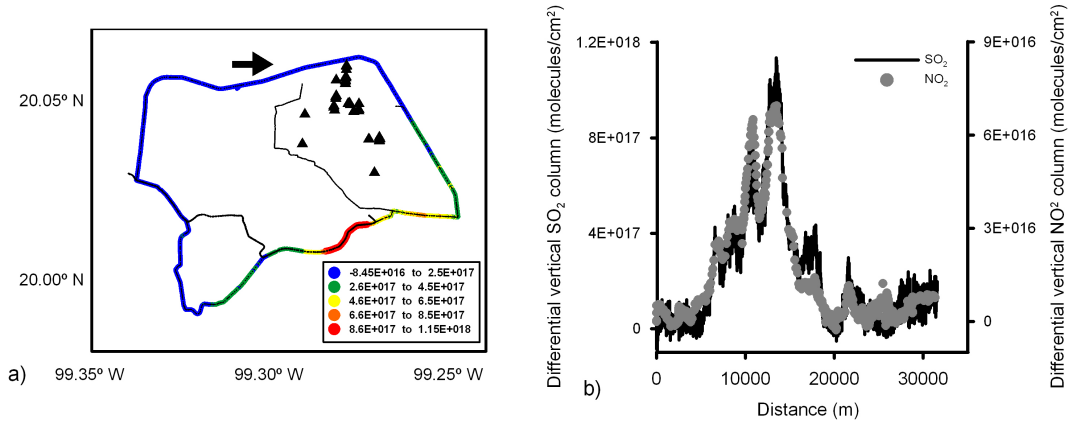

Fig. 3. Typical measurement at Tula industrial complex performed on 26 March 2006 between 14:18 and 15:03 local time. Panel **(a)** presents the spatial distribution of differential SO_2 columns (color coded) quantified during the measurement, whereas panel **(b)** shows variation in differential vertical SO_2 (black) and NO_2 (grey) columns for the measurement as function of travelled distance. The arrow in panel (a) shows the starting point of the measurement and points towards the direction of travel.

3 Results and discussion

3.1 Meteorological conditions

Meteorological conditions in the Tula industrial complex were variable during the monitoring period. From 23 March 2006 a cold surge over the Gulf of Mexico produced strong northerly winds persisting for two days (Fast et al., 2007). Cold surges are a characteristic feature in Central Mexico, bringing cold humid air south into the MCMA. This leads to reduced vertical mixing and increased rain and cloudiness. After the cold surge, conditions in the basin remained humid with weak southward transport at night and afternoon convection events until the end of March (de Foy et al., 2008). During April, most of the days were clear or partly cloudy without rain due to a persistent high pressure system.

Wind speeds were higher during the first days of the field campaign and less intense at the end. Minimum wind speeds were recorded during night time and early morning hours while maximum values were recorded between 19:00–20:00 local time. Maximum temperatures occurred between 16:00–17:00 and minimum temperatures between 07:00–08:00 local time. Relative humidity followed an expected behavior with a maximum during night time and a minimum coinciding with high temperatures. Wind direction before 09:00 was from south-southeast, a transition period was systematically observed between 09:00–11:00 when northerly winds appeared. After midday, wind direction turned from north-northwest to north to north-northeast and this condition was maintained until 22:00 where winds turned again from south-southeast until 9:00 hours of the next day. This cycle was continually observed over the entire measurement period.

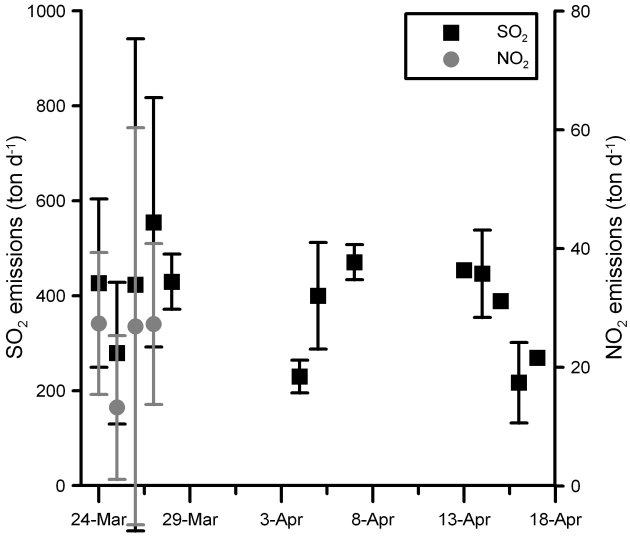

Fig. 4. Daily averages of SO_2 and NO_2 emissions from Tula industrial complex. Vertical lines represent standard deviation, referring to the variability within single measurements conducted during the same day.

3.2 Observed emission factors

A typical measurement around the Tula industrial complex for 26 March 2006 is depicted in Fig. 3. Figure 3a shows the spatial distribution of differential SO_2 columns (color coded) quantified during the measurement. The measurement was conducted between 14:18 and 15:03 local time. The known emission sources located inside the measurement circuit are shown with black triangles. Figure 3b shows the differential SO_2 and NO_2 columns quantified during the measurement, which follow each other during the entire measurement. The

Table 1. Summary of measurements at Tula industrial complex.

Date	NO_2 transects	NO_2 emission (tones day^{-1})[a]	SO_2 transects	SO_2 emission (tones day^{-1})[a]
24 March 2006	2	27±12	3	427±177
25 March 2006	4	13±12	5	279±149
26 March 2006	11	27±33	28	423±518
27 March 2006	10	27±14	26	554±263
28 March 2006			4	430±58
4 April 2006			2	230±34
5 April 2006			5	400±112
7 April 2006			5	470±37
13 April 2006			1	454
14 April 2006			5	446±92
15 April 2006			1	389
16 April 2006			10	217±85
17 April 2006			1	269
TOTAL	*27*	…	*96*	…

[a] The standard deviation refers to the variability of single measurements conducted during the same day and not to the uncertainty of the measurements per se.

Table 2. SO_2 and NO_x emission inventories and NO_2 measurements of Tula industrial complex.

Year	SO_2 (tpy)	NO_x (tpy) [a]	Point Sources	Reference
1999	356 966	37 834	Tula-Vito-Apasco industrial complex	SEMARNAT-INE (2006) [b]
2002	158 330	15 040	Power plant only	Miller and Van-Atten (2004); Vijay et al. (2004)
2003	145 000	–	Tula-Vito-Apasco industrial complex, 2003	de Foy et al. (2007)
2005	112 934 [c]	24 259	Stack emissions from Pemex refinery and Power Plant	SEMARNAT (2008)
2006	135 232	5697	Total emission from Pemex refinery	PEMEX (2006)
2006	140 046 ±37 533	8647 ±2549	Tula-Vito-Apasco industrial complex	This study 2006

[a] Emission inventories give values of NO_x whereas measurements conducted during the field campaign give NO_2 values.
[b] NO_x and SO_x reported emissions for Hidalgo State from point sources where power generation facilities and refineries are the main contributors.
[c] SO_x emissions.

traverse started at the north-western part of the Tula industrial complex (black arrow in Fig. 3a) and continued towards the east. A main peak was found during the traverse at the southeast from the known sources. This measurement yielded an emission of 44 906 kg/h of SO_2 and 2210 kg/h of NO_2. Figure 4 shows a daily average time series of NO_2 and SO_2 emissions calculated from the conducted measurements during the field campaign. In addition Table 1 shows a summary of all the measurements performed during the field campaign. NO_2 emissions were measured between 24–27 March, and SO_2 emissions were quantified between 24 March–17 April 2006.

A total number of 96 transects were performed in order to determine the emissions of SO_2 and NO_2 in the region. Actual emission variations due to changes in the processes, as well as atmospheric perturbations along the measurements in a particular transect are mainly responsible for the observed variation in the estimated fluxes. From the statistical point of view, the larger the number of transects measurements, the better the flux determination.

During MCMA 2006, SO_2 emissions from Tula's industrial complex yielded 384±103 tons day^{-1}; and NO_2 emissions accounted for 24±7 tons day^{-1}. Both SO_2 and NO_2 quantified emissions present large standard deviations, and SO_2 emissions are an order of magnitude larger than the quantified NO_2 fluxes. The high variability on the flux determinations is associated to the actual emission variation on the SO_2 sources in the region, as well as to the uncertainty associated to the wind field at the specific time of the measurements.

In order to give insight as to whether emissions from the Tula industrial complex during the period of this study had any influence on the air quality of the MCMA, data from the Ambient Air Monitoring Network (Red Automática de Monitoreo Atmosférico, RAMA) was accessed online (http://www.sma.df.gob.mx/simat/). During the period of this study, no extraordinary levels of SO_2 and NO_2 (1-h average data), that would lead to exceedance of the Mexican Norms, were registered by the network. However, Concentration Field Analyses using backward trajectories calculated from some of the RAMA sites during the MCMA 2006 field campaign point towards the Tula industrial complex as a potential source area of SO_2 for the MCMA (de Foy et al., 2009).

3.3 Comparison with emission inventories

Table 2 shows a comparison of our results with published emission inventories. In order to develop the first National Inventory of Emissions in Mexico (base year 1999), a multidisciplinary effort between national and international institutions was made. As part of this inventory, PEMEX provided most of the information regarding combustion and process emissions. As for emissions from power generation plants, data was provided by Mexico's Energy Secretariat (SENER). Almost 70% of emissions from combustion were calculated using emission factors from U.S. EPA, 1995, section 1 (AP-42), and the rest were based on measurements reported by the power stations themselves (SEMARNAT-INE, 2006).

Vijay et al. (2004) and Miller and Van-Atten (2004) estimated emissions from power generation plants based on fuel consumption and energy generation data provided by SENER as well as emission factors for specific power generation plants. The methodology used followed the

recommendations of the Emissions Inventory Improvement Program of the US EPA; the emission factors used were obtained from the EPA's AP-42 (1998).

During MCMA 2003 field experiment, SO_2 emissions from the Tula-Vito-Apasco industrial complex were quantified using zenith sky UV spectroscopy, the same technique applied in this study.

The Mexican Environment and Natural Resources Secretariat (SEMARNAT) provided emission data for 2005, based on DATGEN (General Data). DATGEN is a database containing emissions inventories information (principally from combustion processes) from fixed sources of federal and state jurisdiction, located in areas where air quality management plans have been developed.

Surprisingly, regardless the difference in emission determination approaches applied, both SO_2 and NO_2 emissions quantified by the DOAS technique are comparable with emission inventories reported, particularly those after the year 2002. In the Sustainable Development Annual Report (2006), the Mexican Petroleum Oil Company (PEMEX) informs an annual average reduction of 6.3% of emissions into the atmosphere during the period 2001–2006 in the company (PEMEX, 2006). Assuming that this annual average rate applies also for the MHR, current emissions reported in 2006 are consistent with those reported in 1999 (approximately 40% in reduction in six years).

Because almost 100% of the sulfur content in fuels is emitted as SOx, uncertainty on the reported emissions by the Mexican industries applying the AP-42 emission factors is considered to be low. This may be the reason for the accordance of SO_2 reported emissions and measurements.

It is important to note that emission inventories are given in NO_x while our instruments quantify NO_2. The knowledge of the NO_2/NO_x ratio is then important in order to derive NO_x emissions from our measurements. Because of the well known reactions in which NO is oxidized to NO_2 in plumes exiting the stacks of industrial facilities (Finlayson-Pitts and Pitts, 2000), we therefore may assume that the quantified NO_2 represents only part of the total released NO_x and the discrepancies between NO_x inventories and quantified NO_2 may be partially explained by the amount of NO that has not yet been oxidized.

3.4 Comparison of measured and modeled plumes

Comparisons between measured and simulated emissions from the Tula industrial complex were made for 26 March 2006 (Fig. 5) and 4 April 2006 (Fig. 6). On 26 March, according to the DOAS measurements, the plume from the industrial complex was continuously shifting: early in the morning the plume dispersed towards the east, moving towards the southsoutheast by noon and turning back towards the southeast by late afternoon. This is correctly simulated by the model, with the plumes initially moving to east, and then turning to the south and back towards the east again. There are slight differences in the timing and strength of the shifts. The model is not able to represent the split plume at 11:55 with one part going east and the other south, although this is to be expected as these features are smaller than resolution of the wind simulations (3 km grid cells, output every 1 hour). At 14:18, the simulated plume is much narrower than the measurements, suggesting that there is insufficient dispersion in the model. As the spatial and temporal scales of this are below the resolution of the model, this suggests that turbulent mixing should be increased in the trajectory simulations. On 4 April, a wide plume was observed at noon, gradually narrowing towards the afternoon. In general, the plume was moving straight to the southwest throughout the day. This was correctly represented in the model, including the narrowing of the plume as the winds became stronger and the transport faster. In summary, there is good agreement between the measured and simulated plumes suggesting that the model is capable of representing the plume transport, and that the measurements correctly captured the entire plume.

4 Conclusions

Calculated emissions from Tula's industrial complex during the MCMA 2006 field campaign yielded an average of 384 ± 103 tons day^{-1} for SO_2 and 24 ± 7 tons day^{-1} for NO_2. These emissions are comparable to the more recent emission inventories, but lower than the inventories from 1999 and earlier. According to the inventories, SO_2 emissions show average reduction over the years (approximately 40% in six years) and compare well with 2006 emissions reported by PEMEX for the MHR (PEMEX, 2006). On the other hand NO_2 calculated emissions show lower values than previous NO_x emission inventories. This discrepancy may be explained by an incomplete oxidation of NO to NO_2. An important outcome of this study is the fact that our measurements are in good agreement with values reported in recent inventories, implying that the use of emission factors for determination of emissions from power plants and refineries, is an adequate procedure when reliable information of energy consumption and power generation is available.

Although, during the period of this study no extraordinary levels of SO_2 and NO_2 (1-h average data), were registered on the northern part of the MCMA by the Ambient Air Monitoring Network, Concentration Field Analyses using backward trajectories calculated from some of the RAMA sites during the MCMA 2006 field campaign point towards the Tula industrial complex as a potential source area of SO_2 for the MCMA (de Foy et al., 2009).

In addition, the industrial plumes were simulated with forward particle trajectories using the measured emission rates. The good agreement between the simulated plume transport and the column measurements suggests that the model is capable of reproducing dispersion from the Tula industrial zone and brings supporting evidence that the column

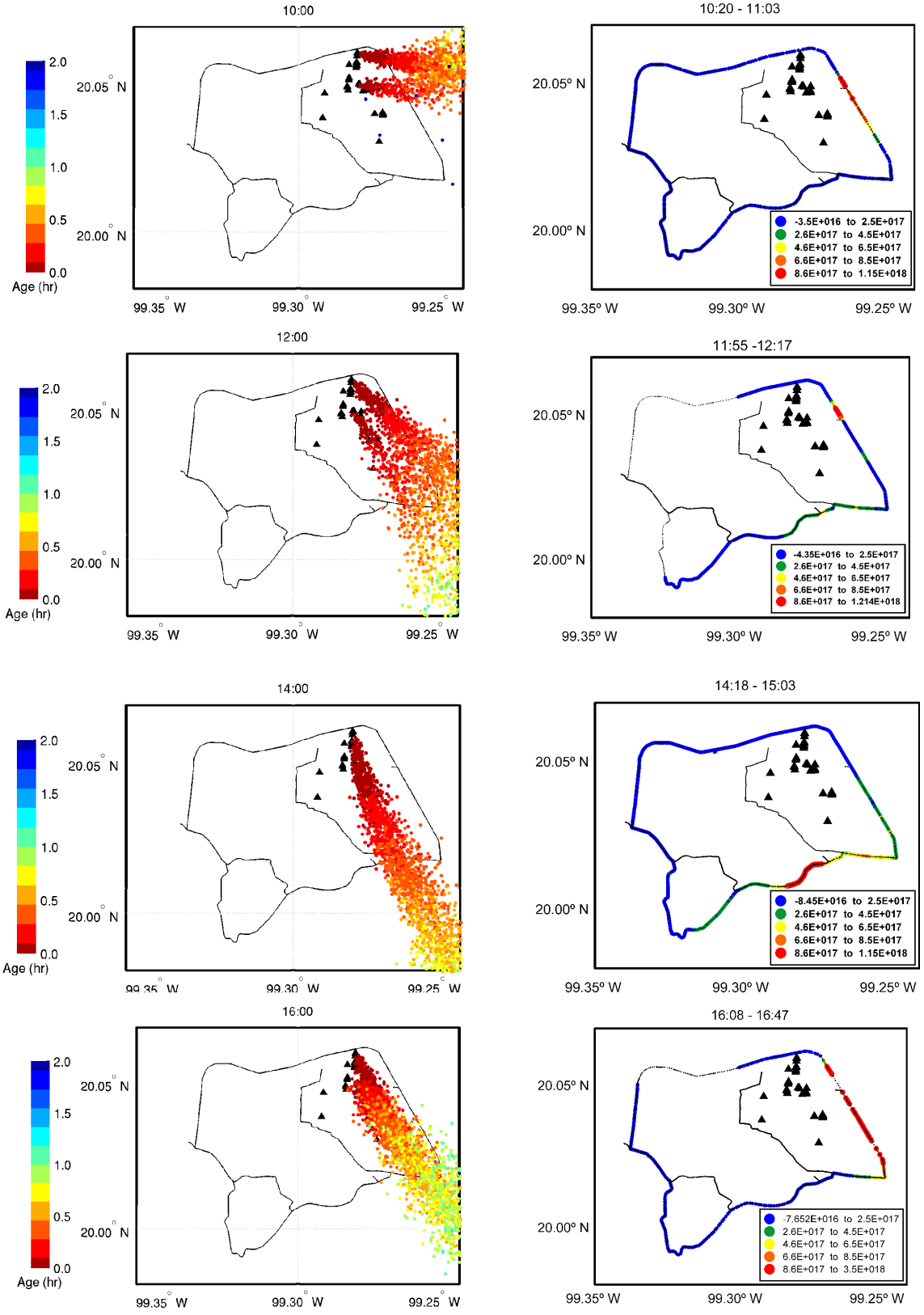

Fig. 5. Comparison between modeled plumes (left) and observed spatial distribution of SO_2 columns (right) during 26 March 2006. Known sources of the power plant and refinery are shown with black triangles. The units of the differential vertical SO_2 columns are molecules/cm^2.

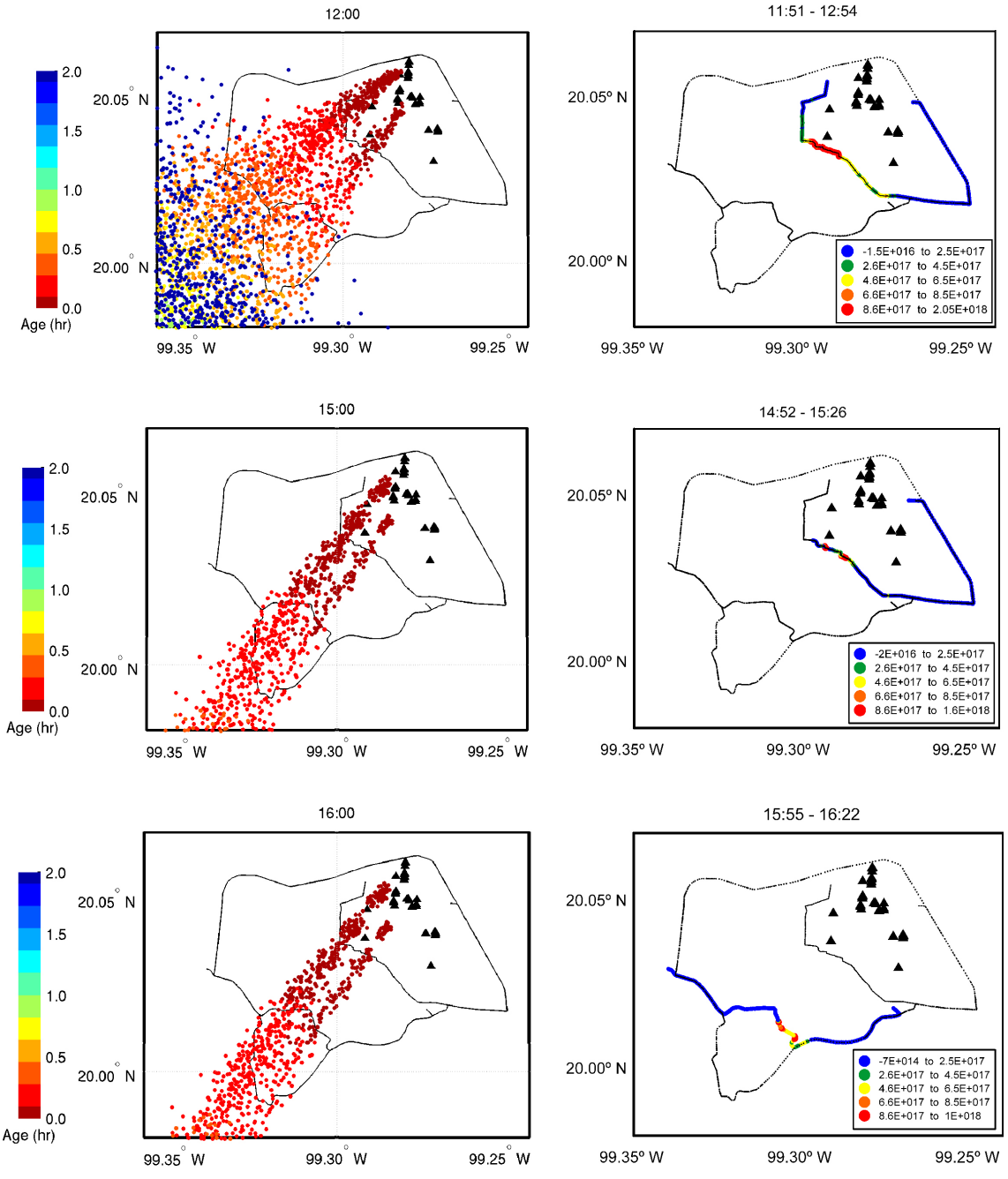

Fig. 6. Comparison between modeled plumes (left) and observed spatial distribution of SO_2 columns (right) during 4 April 2006. Known sources of the power plant and refinery are shown with black triangles. The units of the differential vertical SO_2 columns are molecules/cm^2.

measurements correctly captured the plume. A remaining question is the large standard deviation of the measurements performed during the field campaign. It is thought that the reasons for them are associated with changes in real emissions from the refinery and power plant, as well as unavailability of wind fields at the exact time of every measurement. Variability in fluxes could be caused by plume meandering as well. Both simulations and observations during March attest for plumes shifting over short periods of time, coinciding with measurement days where the largest standard deviations in emissions were found. Quantified emissions during April show less standard deviation, coinciding with more defined plumes. Detailed information about production and performance of the Miguel Hidalgo refinery and the Francisco Pérez Ríos power plant during the field campaign would yield an improved comparison between our measurements and reported values.

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