Atmos. Chem. Phys. Discuss., 9, 5153–5176, 2009
www.atmos-chem-phys-discuss.net/9/5153/2009/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal *Atmospheric Chemistry and Physics (ACP)*. Please refer to the corresponding final paper in *ACP* if available.

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

C. Rivera[1], G. Sosa[2], H. Wöhrnschimmel[3], B. de Foy[4,5], M. Johansson[1], and B. Galle[1]

[1]Department of Radio and Space Science, Chalmers University of Technology, 41296 Gothenburg, Sweden
[2]Matemáticas Aplicadas y Computación, México, Instituto Mexicano del Petróleo, 07730 Mexico, D.F., Mexico
[3]Instituto Nacional de Ecología, 04530 Mexico D.F., Mexico
[4]Molina Center for Energy and the Environment, CA, USA
[5]Department of Earth and Atmospheric Sciences, Saint Louis University, MO, USA

Received: 18 January 2009 – Accepted: 2 February 2009 – Published: 25 February 2009

Correspondence to: C. Rivera (claudia.rivera@chalmers.se)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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 total 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 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 fluxes in the plume. According to our measurements, calculated average flux emission for SO_2 and NO_2 were 155±120 and 9±8 ktons per year, 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. These values are in good agreement with available datasets and with simulated plumes.

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 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 degrada-

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tion 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 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

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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 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. In this case, passive DOAS using scattered sunlight in Zenith Scattered Light mode has been applied. The

key components of passive DOAS instruments are: spectrometer, detector, receiving optics (telescope), additional electronics and computer. Additional software to control the system and perform evaluations is needed, as well as databases of the absorption cross sections of the species to measure (Platt and Stutz, 2008).

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. Traverses of the plume using a mini-DOAS instrument installed on a mobile platform were performed. The instrument is referred to as mini-DOAS due to its small size and low weight. The 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., 2002b). 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., 2002a, 2003a, b, 2006; McGonigle et al., 2002, 2003; Mori et al., 2006; O'Dwyer et al., 2003), industries (McGonigle et al., 2004; Rivera et al., 2009) and cities (Johansson et al., 2008).

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. Afterwards a non-linear fitting of a reference spectrum to the measured spectra is made, in this way obtaining the total column of the gases of interest. 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 (Voigt et al., 2001) cross section was included in the fitting procedure as well.

The mini-DOAS instrument is complemented with a Global Positioning System (GPS), both of them connected to a laptop computer and controlled by custom-built software (MobileDOAS, Chalmers University) which collects and evaluates acquired

spectra in real time. Measurements were performed traversing the plume, at different distances from the source, perpendicular to the plume direction. 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 total columns by the distance traversed perpendicular to the wind direction, and the wind speed at plume height. The total column is defined as the integral of the species of interest along one line (the average concentration of the species times the length of the path). The corresponding methods for obtaining meteorological information are discussed in the following.

2.2 Meteorological measurements

For accurately quantifying emissions, the 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 an IMP site (Longitude 99° 16′ 24.4″ W and Latitude 20° 2′ 48.6″ N), located inside the refinery 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 was 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 known 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 and the ascent rate, and 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 8, 12, 15 and 18 h (local time) by using 300 gr 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 winds 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 from a height of 70 to 80 m and 30 to 50 m respectively, to account for stack height variations as well as variable plume rise.

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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 first 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 where northerly winds appear. After midday, wind direction turned from north-northwest – north – north-northeast and this condition was maintained until 22:00 where winds turned again from south-southeast until 09:00 h of the next day. This cycle was continually observed over the entire measurement period.

3.2 Observed emission factors

A typical measurement of SO_2 and NO_2 columns in the Tula industrial complex is depicted in Fig. 3 for 26 March 2006. 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 se-

ries of NO_2 and SO_2 emission fluxes 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 flux emission 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 transects are main responsible factors of the flux emission variation. 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 17 786±13 779 kg/h. NO_2 emissions accounted for 1044±970 kg/h. Both SO_2 and NO_2 quantified emissions present large standard deviation, 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.

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 power generation plants emissions, data was provided by Mexico's Energy Secretariat (SENER). Almost 70% of emissions from combustion were calculated using emission factors from US EPA, 1995, Sect. 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

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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).

In spite of the industries in Mexico reporting SO_2 emissions applying the AP-42 emissions factors, uncertainty on these values is low, because almost 100% of the sulfur content on fuels is emitted as SO_x. This may be the reason why 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 h). 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 more direct 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.

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4 Conclusions

Calculated emissions from Tula's industrial complex during the MCMA 2006 field campaign yielded an average of 155.8±120 ktpy for SO_2 and 9±8.5 ktpy for NO_2. These emissions are comparable to the more recent emission inventories, but lower than the inventories from 1999 and earlier. 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. The plume was 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 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 and diagonal transects as well. Quantified emissions during April show less standard deviation, coinciding with more defined plumes. Both simulations and observations during March attest for plumes shifting over short periods of time. 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, however it was not available.

Acknowledgements. This work was partly funded by the Comisión Ambiental Metropolitana, the Alliance for Global Sustainability, the Swedish International Development Cooperation Agency, the US National Science Foundation (awards ATM-0511803 and ATM-0810950), the Molina Center for Strategic Studies in Energy and the Environment, and the Mexican Oil Company, PEMEX. The participation of technical staff and students is highly acknowledged: Felipe

Angeles, Olivia Rodríguez and Ana Lilia Alonso. We acknowledge SEMARNAT for providing validated emissions data.

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Table 1. Summary of measurements at Tula industrial complex.

Date	NO_2 transects	NO_2 emission (kg/h)[a]	SO_2 transects	SO_2 emission (kg/h)[a]
24 Mar 2006	2	1140±499	3	17 771±7388
25 Mar 2006	4	551±505	5	11 625±6214
26 Mar 2006	11	1121±1394	28	17 628±21 596
27 Mar 2006	10	1136±565	26	23 101±10 942
28 Mar 2006			4	17 899±2425
4 Apr 2006			2	9575±1429
5 Apr 2006			5	16 666±4685
7 Apr 2006			5	19 604±1542
13 Apr 2006			1	18 909
14 Apr 2006			5	18 596±3838
15 Apr 2006			1	16 204
16 Apr 2006			10	9037±3534
17 Apr 2006			1	11 216
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.

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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	155 803±120 702	9142±8496	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.

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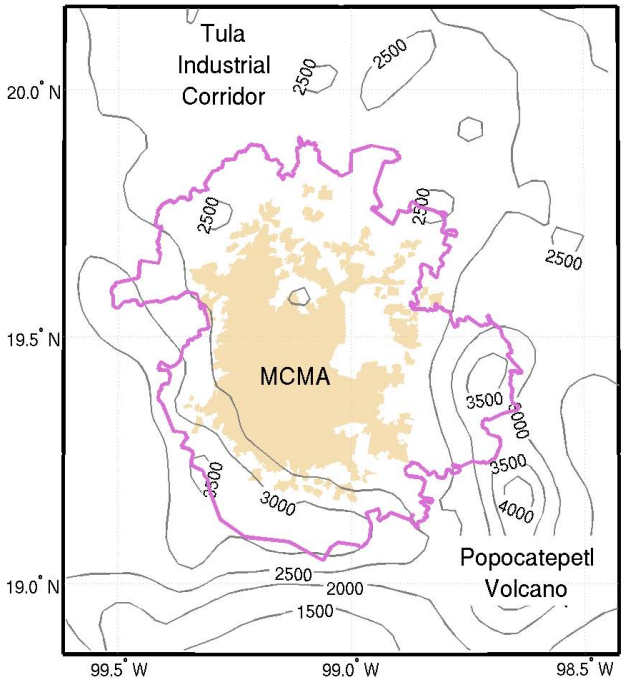

Fig. 1. Location of the Tula industrial corridor, urban area of the MCMA in beige. Terrain contours every 500 m.

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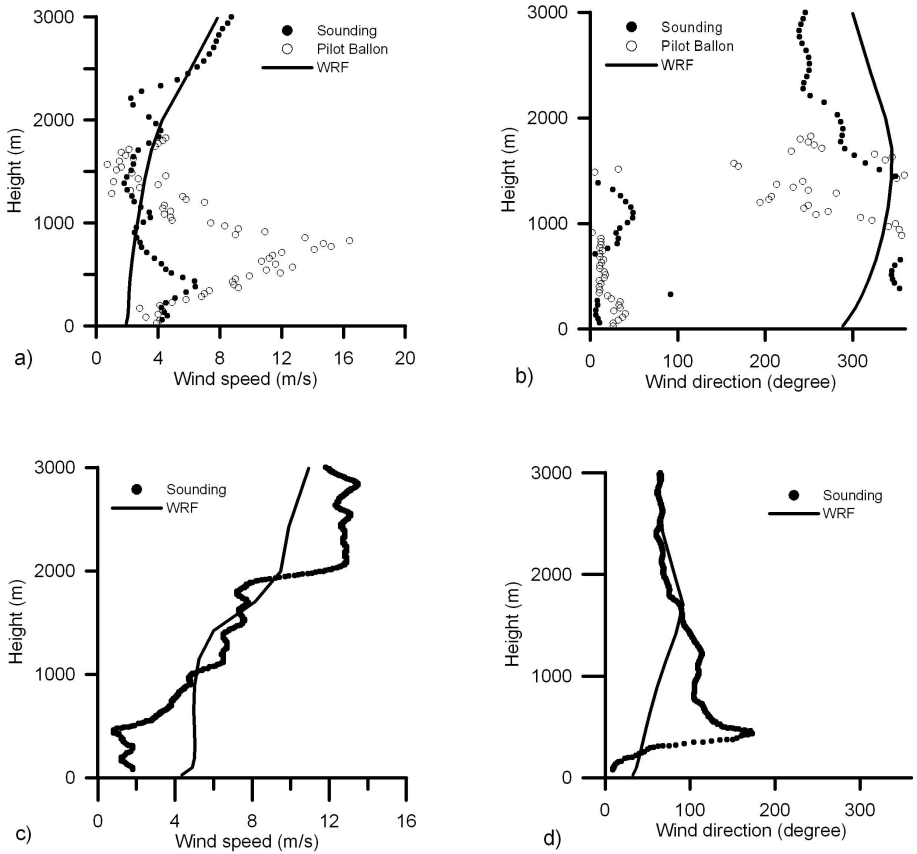

Fig. 2. Wind speed **(a)** and wind direction **(b)** comparison between pilot balloon, sounding and WRF on 26 March 2006. Sounding and pilot balloon were launched at 15:00 and 15:15 local time respectively. Additionally wind speed **(c)** and wind direction **(d)** results from a sounding launched on 4 April 2006 at 12:00 local time are presented together with WRF results.

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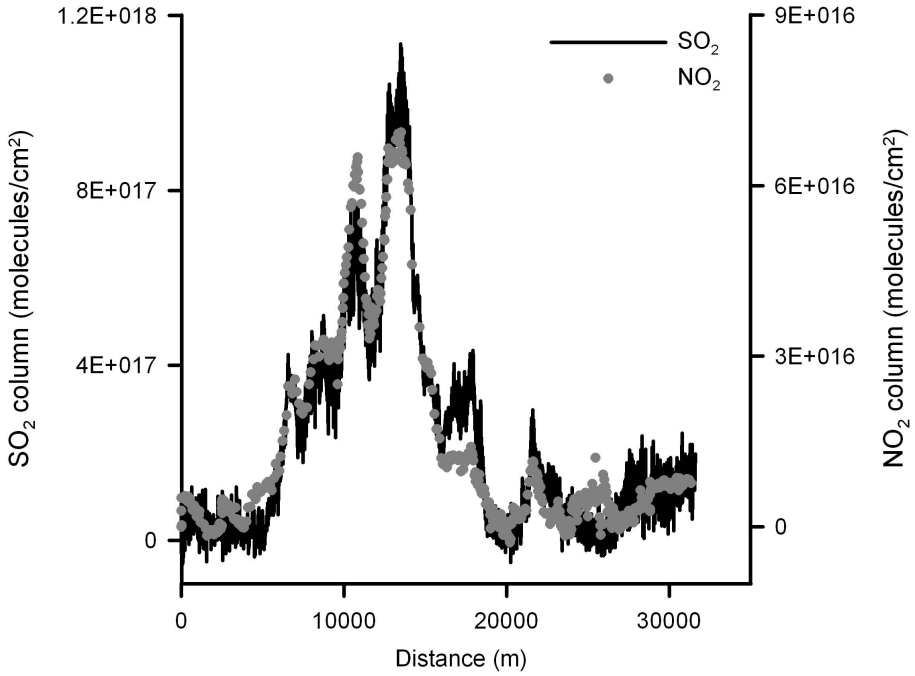

Fig. 3. Typical measurement at Tula industrial complex performed on 26 March 2006 between 14:18 and 15:03 local time (20:18–21:03 UTC). The figure shows variation in vertical SO_2 (black) and NO_2 (grey) columns for the measurement as function of travelled distance.

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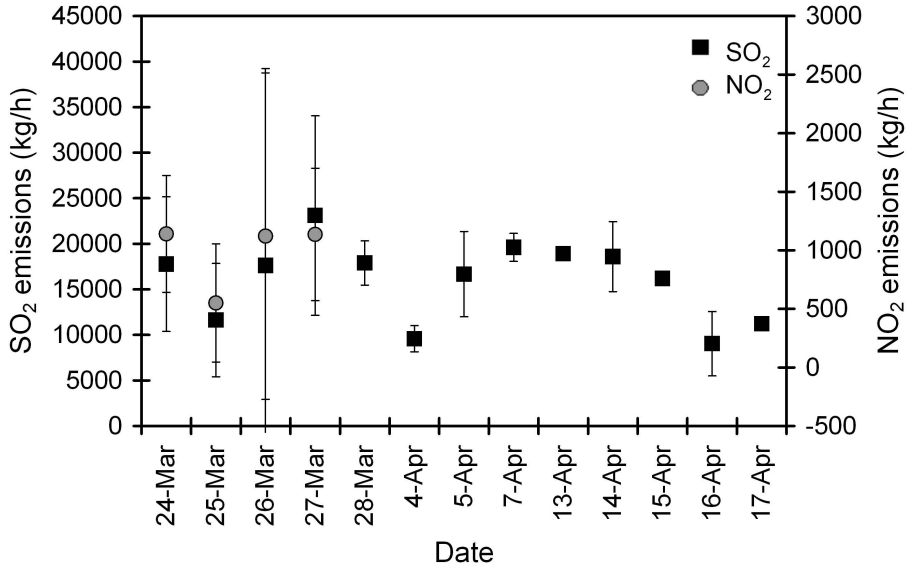

Fig. 4. Daily averages of SO_2 and NO_2 emissions from Tula industrial complex. Vertical lines represent standard deviation, referring to the variability within single measurements conducted during the same day.

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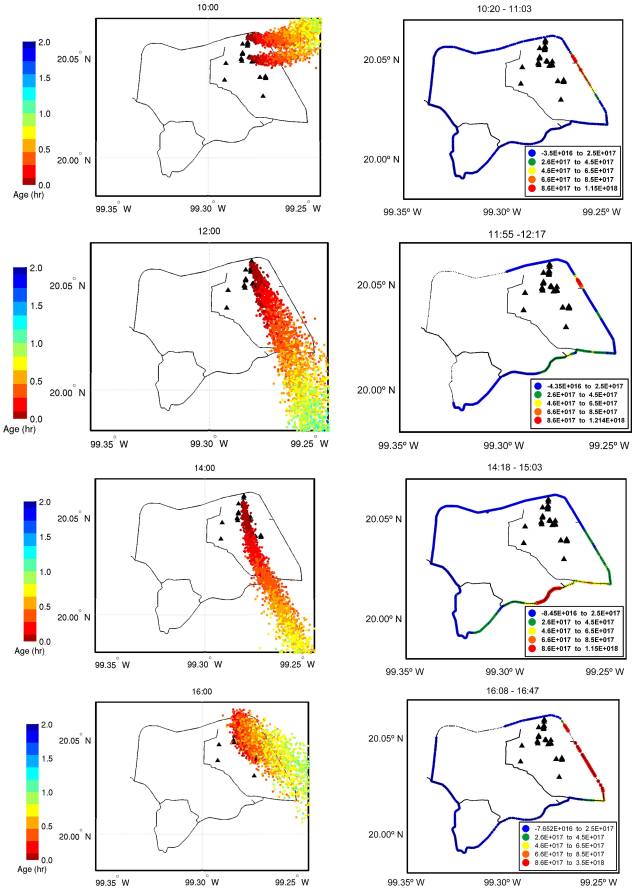

Fig. 5. Comparison between modeled plumes (left) and observed spatial distribution of SO_2 columns (right) during 26 March 2006. Known sources of the power plant and refinery are shown with black triangles.

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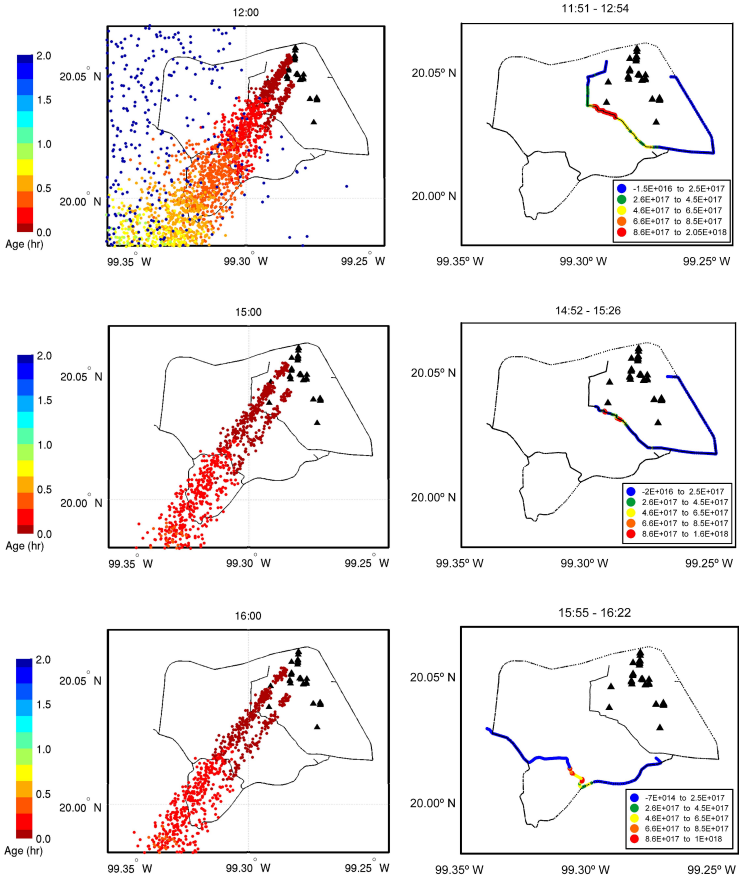

Fig. 6. Comparison between modeled plumes (left) and observed spatial distribution of SO_2 columns (right) during 4 April 2006. Known sources of the power plant and refinery are shown with black triangles.

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