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Modeling results of atmospheric dispersion of NO_2 in an urban area using METI–LIS and comparison with coincident mobile DOAS measurements

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ABSTRACT

Synergetic use of in–situ measurements, remote sensing observations and model simulations can provide valuable information about atmospheric chemistry and air quality. In this work we present for the first time a qualitative comparison between modeled NO_2 concentrations at ground level using dispersion model METI–LIS and tropospheric NO_2 columns obtained by mobile DOAS technique. Experimental and modeling results are presented for a Romanian city, Braila (45.26°N, 27.95°E). In–situ observations of NO_2 and meteorological data from four ground stations belonging to the local environmental agency were used to predict the concentration of NO_2 at ground level by atmospheric dispersion modeling on two days when mobile DOAS measurements were available. The mobile DOAS observations were carried out using a UV–VIS spectrometer mounted on board a car. The tropospheric Vertical Column Density (VCD) of NO_2 is deduced from DOAS observations. The VCD was obtained using complementary ground and space observations. The correlation between model and DOAS observations is described by a correlation coefficient of 0.33. Also, model results based on averaged in–situ measurements for a period of 5 years (2008–2012) are used for an overview of the background NO_2 evolution in time and space for the selected urban area.

Keywords: *Air quality, urban pollution, nitrogen dioxide, model simulations, remote sensing*

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1. Introduction

Nitrogen dioxide (NO_2) is one of the major atmospheric pollutants, with important impact on the air quality. NO_2 is formed naturally in the atmosphere by lightning and microbial activity in soil by the oxidation of ammonium nitrate (Lee et al., 1997; Dunlea et al., 2007). NO_2 also affects the formation of ground–level ozone (O_3), and the concentration of NO_2 is determined by its emission and by its formation via chemical reaction involving NO with O_3 (Song et al., 2011; Shon et al., 2012). NO_2 can react with OH or rain droplets leading to acid precipitation. Anthropogenic emissions originate from fossil fuel combustion, power generation and transport (Ohara et al., 2007). Part of the anthropogenic NO_2 results from the NO caused by tailpipe emissions. Yao et al. (2005) point out that the direct contribution of NO_2 emissions to atmospheric NO_2 pollution is low, since the main component of NO_X emissions is NO, oxidizing to NO_2. In addition, other atmospheric contributions come from non–combustion processes: nitric acid manufacture, welding processes and the use of explosives, etc. (Hanna and Carey, 2010). NO_2 can persist in the atmosphere for several hours to one day (Beirle et al., 2003), lifetime of NO_2 being longer in wintertime due to less OH and increased volume of emissions.

Traffic activity has a significant contribution to NO_2 concentration levels in the urban area (Palmgren et al., 1996; Constantin et al., 2012; Soret et al., 2013; Lee et al., 2014) and is considered to be responsible for over half of NO_X emissions and represents a higher proportion in urban areas (Donnelly et al., 2011). This phenomenon occurs as a result of the increase of primary NO_2 emissions from diesel–fuelled passenger cars (Carslaw et al., 2011; Constantin et al., 2012; Ramachandran et al., 2013) and the non–linear, photochemical reaction of traffic–emitted NO to NO_2 (Sjodin et al., 1996; Meng et al., 2008). NO_2 concentrations near urban traffic routes are often higher than the maximum admitted levels due to the continuous input from road vehicles (Carslaw and Beevers, 2004; Anttila et al., 2011). For instance, NO_2 concentrations in Europe exceeded the annual maximum value in many traffic urban areas in 2009 (EEA, 2009). Since 2010, a new EU limit of the average annual ambient air NO_2 levels has been set up to 40 $\mu g/m^3$ or alternatively the maximum value of 200 $\mu g/m^3$ should not exceed more than 18 hours per year (EC, 2008).

This study uses time series of hourly NO_2 concentrations for the time interval 2008–2012 obtained for the city of Braila from the Local Environmental Protection Agency (EPA). Braila city is considered to be moderately polluted (Constantin et al., 2013a). According to data provided by Braila EPA, more than 50% of NO_2 emissions originate from transportation. While the NO_2 industrial emissions decreased during the last years, due to economic recession, the total NO_2 emission were almost constant. The increasing number of vehicles in Braila city, from 58 335 units in 2008 at 70 700 units in 2012 (DDLVR, 2014), has an important role in the total amount of NO_2. In this paper the spatial and temporal distribution of NO_2 is analyzed using ground–level NO_2 concentrations obtained from measurements, a Gaussian dispersion model, METI–LIS (METI, 2006) and remote sensing observations.

Dispersion models estimate the circulation of pollutants in air and are widely used to calculate the spatial distribution of a pollutant concentration. Dispersion models have been categorized as statistical, deterministic, mathematical and physical modeling (Khare and Sharma, 2002; Odman and Hu, 2010; Carbonell et al., 2013). For the NO_2 model simulations we use the Gaussian dispersion model METI–LIS (Ministry of Economy, Trade and Industry Low Rise Industrial Source). A detailed description of the model and program initialization can be found in the next section.

The aim of the article is two–fold: to evaluate the temporal and spatial evolution of NO_2 concentration using dispersion modeling, by METI–LIS model results for a period of 5 years and to qualitatively compare model results with mobile DOAS measurements. On the one hand, in–situ measurements are performed on a continuous basis, which gives the opportunity to obtain also an overview of the diurnal and seasonal variation of the background NO_2, by averaging over the whole 5–years period. On the other hand, DOAS mobile measurements can be performed only for limited periods of time, thus NO_2 values for only those particular days are needed for the qualitative comparisons.

Experimental data and the methodology are described in Section 2, while the results and discussions are presented in Section 3. Conclusions are given in the last section.

2. Data and Methods

2.1. Observation technique: *in–situ*

Since 2008 the Romanian Ministry of Environment implemented a network of air quality monitoring stations. The National Air Quality Monitoring Network currently consists of 142 fixed monitoring stations, 41 laboratories for analysis endowed with necessary equipment and 42 centers for data processing (Directive 2008/50/EC; EC, 2008). Each monitoring traffic station records, on an hourly basis, meteorological data and concentration of atmospheric pollutants: sulfur dioxide (SO_2), nitrogen oxides (NO_X), carbon monoxide (CO), ozone (O_3), volatile organic compounds (VOCs) and particulate matter. The air quality monitoring network in Braila city consists of four monitoring stations (BR1, BR2, BR3, and BR4) which are localized in different zones (Figure 2) to measure atmospheric emissions and meteorological parameters. For the NO_2 measurements "Thermo scientific model 42i NO–NO_2–NO_X" analyzers, which are based on the most common used technique (chemiluminescence), recommended by the European legislation (European Standard, 2005) are used. This technique involves the reduction of NO_2 to NO using heated (300–350 °C) Molybdenum (Mo) surfaces. Briefly, it is based on the chemiluminescent reaction of NO with O_3 to form electronically excited NO_2, which fluoresces at visible and near infrared wavelengths (Dunlea et al., 2007).

2.2. Observation technique: remote sensing

The remote sensing measurements of the tropospheric NO_2 used in this paper are based on the Differential Optical Absorption Spectroscopy (DOAS) technique (Platt, 1994; Platt and Stutz, 2008; Adame et al., 2012). DOAS is a technique which is widely used on board different mobile platforms like satellites (Bovensmann et al., 1999), aircrafts (Merlaud et al., 2012) or cars (Rivera et al., 2009). The experiment was performed using a mobile DOAS system installed in a car, operated in the framework of a collaboration with BIRA–IASB. The optic system consists mainly of a UV–VIS spectrometer which acquires spectra between 200–750 nm. More details about the mobile DOAS system can be found in Constantin et al. (2013b). The spectra registered during the experiments were analyzed with QDoas software (Fayt et al., 2011), which is dedicated to the spectra analysis measured by the respective instruments. The DOAS analysis gives the Differential Slant Column Density (DSCD) and the tropospheric Vertical Column Density (VCD) of NO_2 is the result of an algorithm which involves ground and space observations (Constantin et al., 2013b). The NO_2 VCD was obtained from the spectra recorded in the zenith geometry, using the procedure introduced by Constantin et al. (2013b). This retrieval procedure of NO_2 VCD is based on the DSCD resulted from the DOAS analysis and involves a Slant Column Density (SCD) reference calculated with the Langley–plot method, a stratospheric VCD obtained from satellite observations and an Air Mass Factor (AMF) calculated with the radiative transfer model (RTM) UVspec/DISORT (Mayer and Kylling, 2005). In brief, the tropospheric VCD can be expressed as:

$$VCD_{tropo} = \frac{DSCD_{meas} + SCD_{ref} - SCD_{strato}}{AMF_{tropo}} \quad (1)$$

2.3. Model Simulation: METI–LIS Model

The NO_2 concentration was simulated using the METI–LIS software (Kouchi et al., 2004), which is a computer–based model developed originally by the Japan Ministry of Economy, Trade and Industry (METI, 2006). The program METI–LIS, model ver. 2.03, is a Gaussian dispersion model and calculates concentrations in steps of one hour or less, therefore a minimum of meteorological data per each hour is necessary (Al Razi and Hiroshi, 2012). This model includes point source, line source, building downwash, terrain effects, and line source emissions. The METI–LIS model adopted a downwash scheme based on that of the US Environmental Protection Agency's (EPA) Industrial Source Complex (ISC) model, but the parameters in the dispersion widths describing the down–wash effect were improved by incorporating the results of wind tunnel experiments (Bowers and Anderson, 1981).

Essential input data are emission rate and other emission conditions such as location, height, gas volume and temperature, and meteorological factors at every hour during the averaging period. The measured hourly NO_2 data–set was processed to match the pattern required by the program and were used as inputs in the model. Wind direction and speed, temperature, solar radiation and atmospheric stability were the meteorological data required for our analysis. Considering that, the recommended format for wind–direction data are compass–point notation (north–north–east: 1; north: 16; calm: 0; missing measurements: 9 999). Wind measurements, clockwise from due north, were converted to the above format before input. Wind–speed data was expressed to 0.1 m/s accuracy. The daytime Pasquill stability category was determined by entering solar radiation data measured with a pyrheliometer and hourly averaged for the time interval. The night stability has been modeled on the assumption that it is solely dependent on wind speed, thus the model uses only wind–direction and wind–speed data for night stability calculations; cloud cover or other input data are not needed.

The purpose of METI–LIS model is to estimate a long–term, average distribution of pollutant concentrations in a relatively large area, such as Braila. Atmospheric concentration dispersion of chemical substances of a 50×50 m square spatial grid for a short or long term can be calculated by this model. Because there is very limited knowledge about the horizontal dispersion widths observed near roadways, this model sets the horizontal dispersion width to the target road width divided by 2.15, as given in the line–source calculation released by the US Environmental Protection Agency (Bowers et al., 1982).

This program can make calculations for point sources (fixed sources of emissions such as factories) and line sources (mobile emission sources, such as traffic). The calculation method selected in our study was for line sources. Input parameters were: object substance (chemical substance name and molecular weight), operation pattern (long–term), meteorology, the line source coordinates (emission rate, road width), receptors, etc.

Sources with line–shaped characteristics are calculated in the model by numerically integrating the point–source plume Equation (2):

$$C(x,y,z)=\frac{Q}{2\pi\sigma_y u}\exp(-\frac{y^2}{2\sigma_y^2})[\exp(-\frac{(z-He)^2}{2\sigma_z^2})+\exp(-\frac{(z+He)^2}{2\sigma_z^2})] \quad (2)$$

where C is the concentration (g/m³), x is the downwind distance from the emission source (m), y is the crosswind distance from the emission plume centerline (m), z is the distance above the ground level (m), Q is the pollutant emission rate (g/s), He is effective plume–rise height, u is wind speed (m/s), σ_y is horizontal dispersion width (P–G curve) (m), σ_z is vertical dispersion width (P–G curve) (m).

3. Results and Discussions

3.1. NO_2 concentrations: seasonal, diurnal and spatial variations for 2008–2012

Measured NO_2 values vary according to the type and position of the observation station and depending upon the source type. As a consequence, a traffic type measuring station will record higher values than an urban station. For the present study, the measured data have derived from the measuring stations which were scattered throughout the city and covered all the locations under observation.

Figure 1 shows the diurnal variation of seasonally averaged concentrations of NO_2, from all stations for each year between 2008 and 2012. The lowest average hourly concentration (6.4 µg/m^3 for 4 LT) was measured in the summer of 2009 and the highest average hourly concentration (41.8 µg/m^3 for 21 LT) was observed in the winter of 2010–2011, when temperatures down to –20 °C were recorded. In this period, the fuel consumption for domestic heating and traffic increased, resulting in a higher NO_2 pollution compared to previous or subsequent years. In Braila there is a wide range of extreme weather events such as those in cold season: polar or arctic cold waves, temperature inversions, frost and hoarfrost the most intense, heavy snowfalls, strong winds, blizzards and heavy snow. In contrast, during the warm season there are hot waves tropical phenomena, dryness and drought and hot dry winds etc (NMA, 2008).

Expectedly, two peaks are observed around 9 LT (Local Time) and 20–21 LT, as a consequence of the "rush hour" traffic, suggesting that a substantial percentage of the NO_2 emissions are mainly due to the traffic. Minimum values are generally recorded in the early morning, between 3 LT and 5 LT. The relative diurnal variation of the NO_2 concentration can reach about 200%. In the first part of the morning the NO_2 concentration is abruptly increases due to traffic/anthropogenic activities (Bralic et al., 2012). Later in the morning, NO_2 concentrations decrease slightly due to reduced traffic but also due to photochemistry. At evening rush hour, the NO_2 content is relatively higher than in the morning and the increase is even more rapid than during morning. NO pattern is observed in the year–to–year variations of NO_2 concentration but during 2008 and 2009 NO_2 is lower and increases during the last three years of the period under investigation.

The diurnal variation of the local NO_2 throughout all seasons shows similarities but also distinct patterns for each season. Morning and afternoon peaks are slightly higher during the autumn and winter seasons than during spring and summer. The amplitude of the diurnal variation is larger during the autumn in comparison to the others seasons. The high level of emissions during cold seasons can be due to increased fossil fuel consumption, photochemistry processes which occur in atmosphere. Variations of the diurnal cycle, with peaks in the morning and afternoon, are clearly related to the variation of traffic load (e.g. increased road transport during the day). Local variations and difference between various months is due to variability in local meteorology, driving conditions, the local traffic condition (e.g. traffic congestion, road work), synchronization of traffic lights, etc.

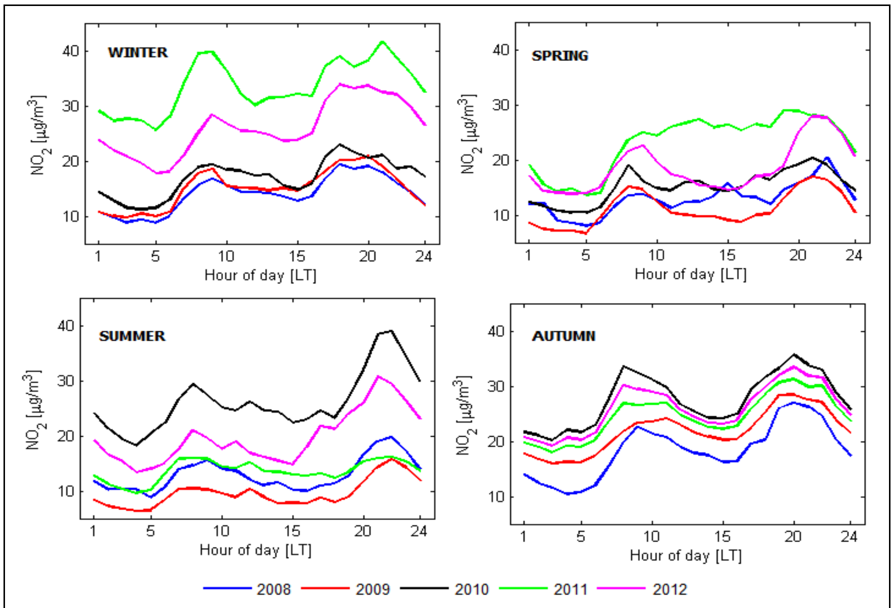

***Figure 1.** Diurnal variation of seasonal averages of NO_2 concentrations for 2008–2012.*

The diurnal variation is the spring and summer of 2011 is different, with no clear peak and a constant high value of the NO_2 over the entire day. There is no clear cause for this particular behavior. We investigated the associated variation of meteorological features but no particular feature appeared for 2011 that could explain a natural cause of the particular behavior in 2011. One possible cause might be linked to street works/roads closure.

In Romania, where anthropogenic emissions represent a significant percentage of NO_2, (EEA, 2012) concentrations are typically higher in winter and autumn probably due to heating of the residential areas. Winter NO_2 concentrations exceed the summer ones by a factor of roughly 1.5. Lower NO_2 concentrations were particularly recorded during the spring period, which might be explained by precipitation increase during this period. Rain efficiently removes NO_2 from the atmosphere via HNO_3 (Kuenen, 2006).

Figure 2 shows the average spatial distribution of NO_2 concentration for the entire city, from each of the selected years (2008–2012), obtained with the METI–LIS model. Violet areas on the maps indicate the locations where the EU limit values are possibly exceeded.

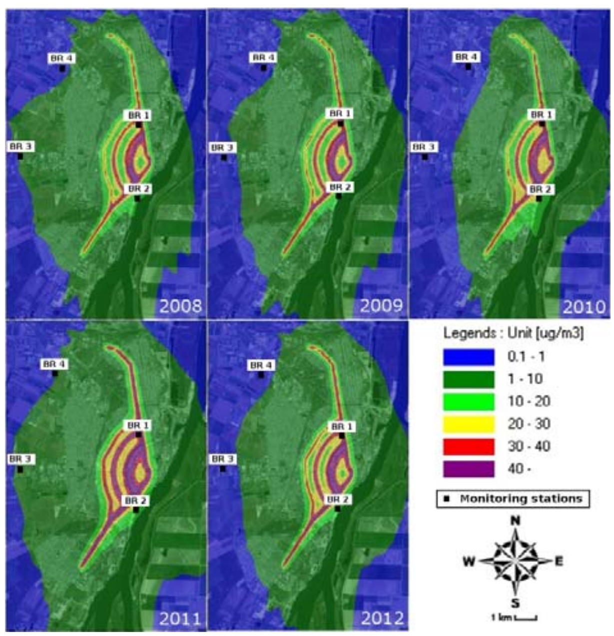

Figure 2. *Dispersion of NO_2 for 2008–2012. NO_2 concentrations between 0.1 and 1 µg/m^3 are shown in blue color, 1–10 µg/m^3 in dark green, from 10 to 20 µg/m^3 in light green, 20–30 µg/m^3 in yellow, 30–40 µg/m^3 in red, and over 40 µg/m^3 in violet. Note that the intense green to the SW of the map is due to the superposition with the dark colors used for the Danube.*

The highest NO_2 concentration is seen, for each year, along the main streets and in their close vicinity, obviously in connection with the traffic. The pollutant concentrations gradually decrease laterally from the roadways. There is no significant variation during the five years at least for the main roads and the general spatial distribution. The polluted area is wider in 2008 and 2009, but smaller in 2012. This is, most likely, an effect of meteorological conditions and is less connected to a reduction of the number of anthropogenic sources, since Figure 1 shows that NO_2 concentration in 2012 is high. The dominant NNE wind in this area carries NO_2 loading to the north of the city in 2009–2011. An important reduction of NO_2 concentration is observed especially at the periphery of the city, to the west. Some side streets, where the pollution level between 2008 and 2010 was low, become heavily polluted in 2011 and tend to be less affected by traffic in 2012.

A careful analysis of the maps reveals the fact that spots of NO_2 appear mostly near cross–roads and, probably, near traffic lights. Roorda et al. (2011) used a Gaussian plume equation to demonstrate that the lateral concentration of the pollutants resulting from traffic decreases rapidly as distance increases. Furthermore, at approximately a lateral distance of ~100 meters from the source, the contribution of the traffic line source to total pollutant concentration was insignificant. This can be seen in our maps, where streets are clearly drawn by their heavy NO_2 imprint.

3.2. Comparison of model simulations with mobile DOAS measurements

In this section we present a qualitative comparison between METI–LIS results and mobile DOAS measurements performed. Mobile DOAS measurements were performed in Braila city on the following days: 27 July 2011 from 12–13 LT and 26 July 2013 between 11–12 LT. All mobile DOAS measurements were performed under clear–sky conditions. The METI–LIS model was run using coincident NO_2 hourly measurements at the same hours as inputs. Note that this comparison aims at comparing mainly spatial variability of NO_2, since DOAS measures total tropospheric column (measured in molec./cm^2) while the model simulates NO_2 concentration at ground level (measured in µg/m^3). One cannot expect a one–to–one coincidence between NO_2 concentration at ground level (map) and the total VCD of tropospheric NO_2 (DOAS). Model results give an average picture of the NO_2 ground–level concentration at the time of DOAS measurement, while DOAS measurements are localized and instantaneous. However, a qualitative comparison can be performed, which might help assessing the capabilities of the model and separating between anthropogenic and natural contributions to NO_2 production.

The comparison between mobile DOAS measurements and METI–LIS for 27 July 2011 and 26 July 2013 is shown in Figures 3 and 4. The left–hand side shows results of DOAS measurements superimposed on the METI–LIS map and the right hand side separates the two data sets. Both sets show higher values along the main routes which cross the city from North to South.

The mobile DOAS measurements used in the present study took place around noon, along various types of roads including roads with low, moderate and intense traffic. They show that, for 27 July 2011, the NO_2 loading increases from the periphery of the city (~5x10^{15} molec./cm^2) to the city centre, where the maximum (~2.5x10^{16} molec./cm^2) is reached. This is somehow in accord with variation of modeled NO_2 concentration, which is exceptionally high along centre roads compared with the outskirts. However, modeled variations are far more abrupt compared to DOAS results. The explanation might be related to the fact that the NO_2 profile is not homogeneous in the city center, where the highest concentration is close to the, then surface dynamic range is higher for ground concentrations than for VCD (Dieudonne et al., 2013). METI–LIS results refer to ground level, where the variation of NO_2 concentration is due almost exclusively to the spatial distribution of pollution sources and also to meteorological state (mostly winds). Secondary smaller increases of the DOAS NO_2 are observed at junctions with heavily polluted roads seen in METI–LIS map. Both model and DOAS show that NO_2 loading increases intermittently along the road.

During the second day of mobile measurements, 26 July 2013, the general characteristics of NO_2 loading are similar to the 1st day. DOAS measurements show a maximum of ~2.3x10^{16} molec./cm^2 close to the city centre and about 5x10^{15} molec./cm^2 close to the periphery. Two spots are observed, with high values of the NO_2 tropospheric column. A close look of the two plots in the right–

hand side in Figure 4 shows that one of these nicely coincides with a maximum concentration given by METI–LIS and the other is seen at a junction with another major road, also heavily polluted according to METI–LIS results. Interestingly, there is a drop in NO_2 loading which is observed in both NO_2 sets, although their exact coordinates are slightly different.

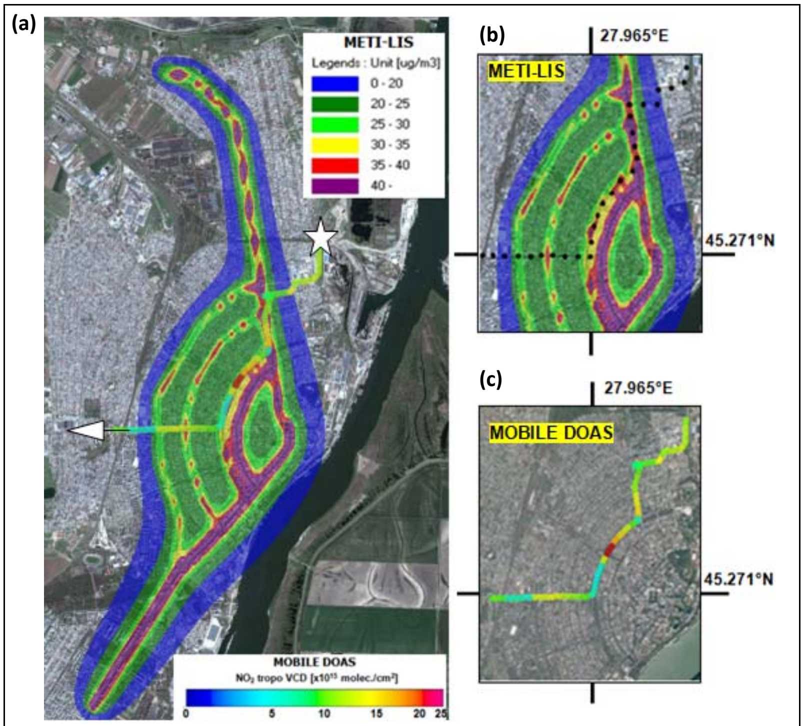

Figure 3. *Comparison between METI–LIS modeled NO_2 concentration and tropospheric VCD of NO_2 retrieved from mobile DOAS observations in the 1st day: July 27, 2011.* ***(a)*** *Results of DOAS measurements superimposed on the METI–LIS map. The star shows the departure point.* ***(b)*** *The METI–LIS map and the trajectory of mobile DOAS (black dots);* ***(c)*** *DOAS measurements.*

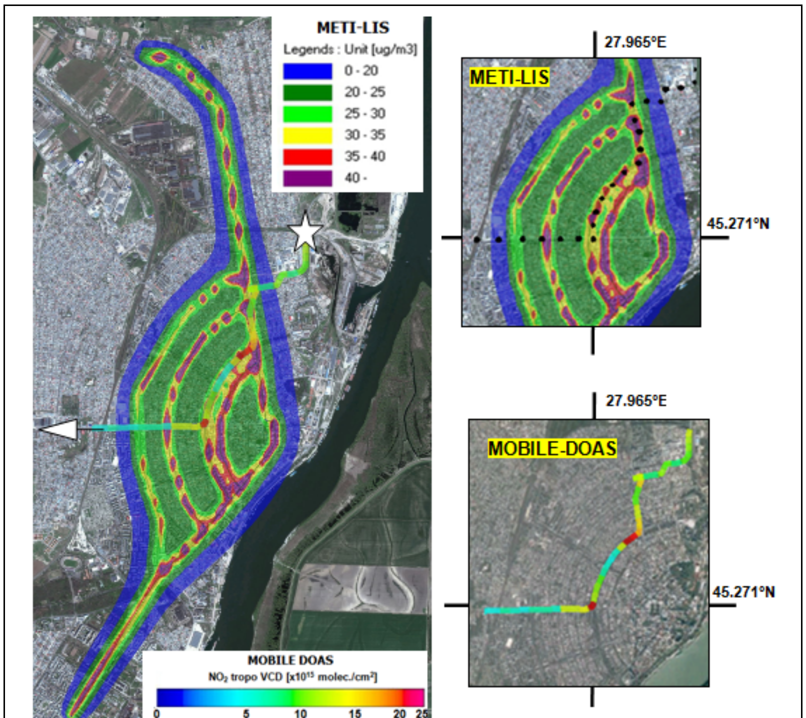

Figure 4. *Similar to Figure 3 for the 2nd day of DOAS measurements: July 26, 2013.*

NO_2 concentrations given by the METI–LIS model along the trajectory of the mobile DOAS were compared with results for the VCD if tropospheric NO_2 obtained from DOAS measurements in Figure 5. Expectedly, differences exist between the two sets, since the model gives an hourly averaged NO_2 concentration at ground level, while DOAS measures the instantaneous variation of the NO_2 total column; however, the resemblance is pretty good. This is supported by a correlation coefficient of 0.33 (p<0.05). Peaks observed by DOAS at various points, in both days (marked with B, D, E, G in Figure 5) are also seen in modeled results. On the other hand, other peaks are seen only in modeled results (C), which might be explained by the fact that DOAS gives local and instantaneous results while the model averages over one hour. Interesting, the minima in METI–LIS are observed also by DOAS (e. g. A, F), in the same spot on the first day and 0.5 km away in the 2nd day. Existing peaks of the NO_2 concentration at specific points, showing up in both DOAS and METI–LIS at junctions or along the roads suggest that: (1) the source of NO_2 peak is anthropogenic and due to traffic, (2) the pollution at these points remains high over the entire day. Differences between the two variations show that NO_2 concentration given by METI–LIS is too low away from the source. NO_2 values measured by DOAS are relatively constant along various roads except of the polluted ones, while METI–LIS shows that NO_2 decreases dramatically away from the main roads.

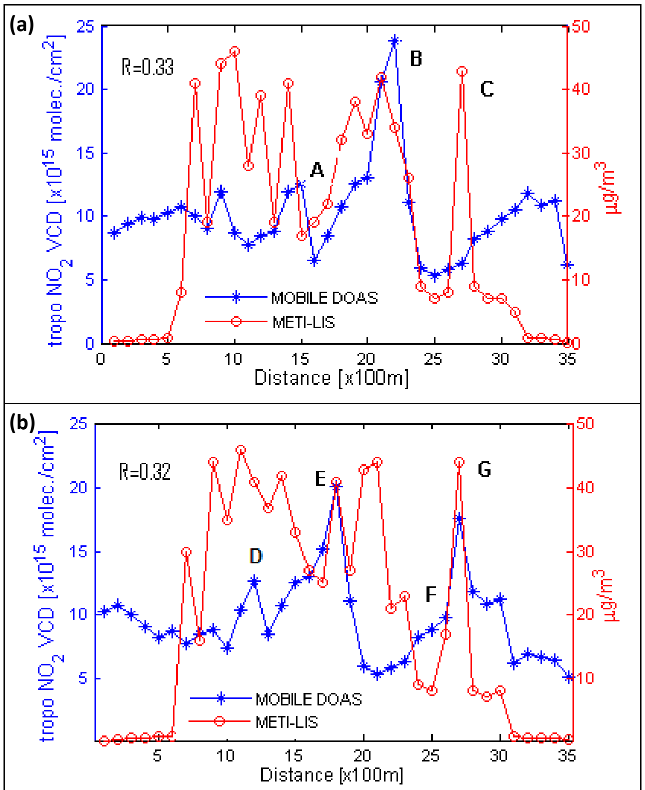

Figure 5. *Comparison between modeled NO_2 resulted from METI–LIS (red) and tropospheric NO_2 from DOAS observations (blue) along the trajectory of the car for the two days:* ***(a)*** *27 July 2011 and* ***(b)*** *26 July 2013.*

4. Conclusions

Results of the METI–LIS dispersion model and hourly NO_2 concentration measured by monitoring station during 5 years (2008–2012), were used to study diurnal, seasonal and annual variation of NO_2 as well as the NO_2 spatial distribution in a medium polluted city. The diurnal variation has peaks at 9 and 21 LT, suggesting that NO_2 has an important anthropogenic source, mainly related to traffic emissions. NO_2 concentration is higher during cold seasons than during warm seasons, which is expected considering anthropogenic emissions and photochemistry. There is some increase in NO_2 concentrations from 2008/2009 to 2011/2012, which is attributable to the increase of the number of cars. However, the increasing trend is not significant in comparison with trends observed in the urban areas of other European countries.

The capabilities of METI–LIS model were tested by comparing model results for two days (27 July 2011 and 26 July 2013) with measurements of the vertical column density of NO_2 on board of a car carrying a DOAS equipment. In the city centre the vertical column density is 2.4x10^{16} molec./cm^2 while METI–LIS gives a daily average ground–level NO_2 concentration of 40 µg/m^3 for the selected days, which are both in summer. Modelled averaged NO_2 concentrations along the trajectory of the car which carried the mobile spectrometer were compared with NO_2 vertical column density. A significant correlation coefficient of 0.33 between METI–LIS and mobile DOAS measurements observations and direct comparison of the two datasets show that METI–LIS model captures part of the instantaneous characteristics of the NO_2 spatial distribution described by DOAS measurements. Results of METI–LIS dispersion model indicates that NO_2 is high along and in the close vicinity of the main streets, but rapidly decreases to the periphery and away from the main roads. Mobile DOAS measurements show similar peaks at points where traffic jams are likely to occur or at junctions between roads with heavy traffic, but a much slower decrease of NO_2 with increasing distance from major roads. The direct comparison also shows that METI–LIS underestimates the NO_2 loading away from the main roads but identifies correctly peaks of NO_2 in various spots along a road with intense traffic. DOAS measures the vertical column density of tropospheric NO_2, comprising a high percentage of naturally produced NO_2, while environmental stations measure the ground–level concentration, where a high contribution from anthropogenic sources exists. Thus one cannot expect a one–to–one coincidence between the two data–sets. However, differences and similarities between these two types of measurements contribute to separating between natural and anthropogenic sources of NO_2 variability.

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