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Comparisons of ground-based tropospheric NO2 MAX-DOAS measurements to satellite observations with the aid of an air quality model over Thessaloniki area, Greece

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Abstract. The main issue arising from the comparison of ground-based and satellite measurements is the difference in spatial representativeness, which for locations with inhomogeneous spatial distribution of pollutants may lead to significant differences between the two datasets. In order to investigate the spatial variability of tropospheric NO_2 within a sub-satellite pixel, a campaign which was lasted for about six months was held at the greater area of Thessaloniki, Greece. Three DOAS/MAX-DOAS systems performed measurements of tropospheric NO_2 columns at different sites representative of urban, sub-urban and rural conditions. The direct comparison of these ground-based measurements with corresponding OMI/Aura and GOME-2/MetOp-A and GOME2/MetOp-B products showed good agreement only over the rural area. GOME2A and GOME2B sensors show an average underestimation of tropospheric NO_2 over the urban area of about $9.12 \pm 7.33 \times 10^{15}$ and $9.58 \pm 8.21 \times 10^{15}$ molecules cm^{-2}, respectively. The mean difference between ground-based and OMI observations is significantly lower ($6.03 \pm 6.04 \times 10^{15}$ molecules cm^{-2}), mainly due to the higher spatial resolution of OMI. OMI data were adjusted using factors calculated by an air quality modelling tool, consisting of the Weather Research and Forecasting (WRF) mesoscale meteorological model and the Comprehensive Air Quality Model with Extensions (CAMx) multi-scale photochemical transport model. This approach resulted to significant improvement of the comparisons over the urban monitoring site. The average negative difference of OMI observations from Phaethon measurements was reduced to $1.15 \pm 6.32 \times 10^{15}$ molecules cm^{-2}.

Keywords: tropospheric NO_2, MAX-DOAS, Phaethon, ground-based, satellite, OMI, GOME-2, air quality modelling, CAMx, Thessaloniki air quality

1 Introduction

Nitrogen oxides ($NO_x = NO + NO_2$) are among the most important trace components of the atmosphere playing a key role in the tropospheric photochemistry [Seinfeld and Pandis, 1998]. They affect the oxidation capacity and the radiative forcing in the lower atmospheric layers by controlling the ozone formation, contributing to nitric acid (HNO_3) and nitrate radical formation and affecting the hydroxyl levels [Solomon et al., 1999; Finlayson-Pitts and Pitts, 2000]. The main emission sources of nitrogen oxides are fossil-fuels combustion, biomass burning, microbiological processes in the soil, lightning and aircrafts [Lee et al., 1997; Jaeglé et al., 2005]. The most important anthropogenic source is the high-temperature combustion processes occurring in vehicle engines and industrial and power plants [EEA report, 2013]. Hence, urban areas, with heavy road traffic, as well as industrial areas are characterized by inhomogeneous spatial and temporal patterns in NO_x concentrations.

Nitrogen dioxide (NO_2) is mainly produced by the oxidation of nitrogen monoxide (NO) and only a small proportion of NO_x is emitted directly as NO_2 [Hewitt and Jackson, 2009]. However, in the case of diesel vehicles the fraction of directly emitted NO_2 to the total NO_x emissions is much higher, resulting in a significant increase of NO_2 emissions and more frequent breaching of NO_2 air quality limits in urban locations in recent years [Grice et al., 2009; Keuken et al., 2012].

Thessaloniki is the second largest city of Greece with a population of more than 1 million inhabitants about 10% of the total population of the country [Resident Population Census 2011]. The main air pollution sources in Thessaloniki are road transport, domestic heating and industrial facilities, while the air quality of the city is affected by the local topographic and meteorological characteristics and regional pollution transport [Poupkou et al., 2011]. NO_2 concentrations in the city tend to stabilize during the last decades with the highest NO_2 levels observed at the traffic hotspots in the center of the city [Moussiopoulos et al., 2008]. According to Zyrichidou et al. [2009] the mean value of tropospheric NO_2 column until 2008 over Thessaloniki was $3.9 \pm 3.8 \times 10^{15}$ molecules cm^{-2} and $4.2 \pm 3.8 \times 10^{15}$ molecules cm^{-2} as observed by GOME-2 and OMI satellite instruments correspondingly.

Well established methods are used worldwide for monitoring NO_2 concentrations based on both in situ measurements from local air quality networks and remote sensing from ground-based instruments and satellite sensors [e.g. Ordonez et al., 2006; Blond et al., 2007; Brinksma et al., 2008]. Space-borne measurements provide information on NO_2 concentrations in a larger scale and over areas, such as oceans and deserts, where ground-based systems cannot be easily deployed. On the other hand, the spatial and temporal resolution of the satellite data is limited by the satellite footprint size and its overpass time respectively. Thus, well-established, extended and relatively dense ground-based networks in areas where significant spatial and temporal variations in NO_2 loading are observed can improve the validation of the satellite data sets.

Remote sensing of NO_2 concentrations is based mainly on the Differential Optical Absorption Spectroscopy (DOAS) analysis [Platt, 1994; Platt and Stutz, 2008] of radiance data, measured either from the space or from the ground. The first studies applying the DOAS method to zenith ground-based measurements for the retrieval of tropospheric and stratospheric NO_2 date back in the '70s [Brewer et al., 1973; Noxon et al., 1975]. In the last few decades, the DOAS analysis has been widely applied in ground-based systems for the monitoring of air quality species like NO_2 in the atmosphere and is considered as a reference technique for the validation of satellite observations [e.g. Celarier et al., 2008; Kramer et al., 2008; Herman et al., 2009; Irie et al., 2012; Li et al., 2013; Ma et al, 2013; Hendrick et al., 2014]. Several studies have shown that satellite sensors underestimate the tropospheric NO_2 levels over regions characterized by inhomogeneous pollution loadings such as urban and industrial locations. Irie et al. [2012] have shown a clear bias of less than 10% between space-borne and ground-based observations over the Tokyo area in Japan, which is characterized by significant spatial variations in NO_2 concentrations. In

Celarier et al. [2008] the correlation coefficient of the comparison of OMI-derived tropospheric NO_2 with different MAX-DOAS instruments at Cabauw, The Netherlands, were found to be about ~0.6. Kramer et al. [2008] estimated similar correlation coefficient between OMI and concurrent MAX-DOAS observations over Leicester, England, while they found significant underestimation of OMI in late-autumn and winter months when comparing with weighted near-surface concentrations.

In this study, tropospheric NO_2 column measurements derived from satellite sensors (OMI/Aura, hereafter OMI, GOME-2/MetOp-A, hereafter GOME2A, and GOME-2/MetOp-B, hereafter GOME2B) are compared with data from MAX-DOAS systems that were deployed in three different sites within the greater area of Thessaloniki, Greece, for a period of a few months. Air quality at these locations, is representative of urban, sub-urban and rural conditions. Adjustment factors calculated by an air quality modelling tool, consisting of the WRF meteorological model and the CAMx air quality model, are applied to satellite data in order to minimize the deviation from ground-based data arising from differences in the spatial representativeness of the two data sets.

2 Observations of NO_2 in the greater Thessaloniki area

2.1 The Phaethon system

Phaethon is a miniature ground-based MAX-DOAS system that performs fast spectrally resolved measurements in the wavelength range 300-450 nm which are used for the retrieval of total and tropospheric columns of atmospheric trace gases. The prototype system was developed in 2006 at the Laboratory of Atmospheric Physics (LAP) in Thessaloniki, Greece [Kouremeti et al., 2008; Kouremeti et al., 2013]. Phaethon has been upgraded recently to improve its performance and two new clone systems have been assembled. The system comprises a cooled miniature CCD spectrograph (AvaSpec-ULS2048LTEC) by Avantes (http://www.avantes.com/), the entrance optics and a 2-axis tracker.

The spectrometer is a symmetrical Czerny-Turner type with 75 mm focal length and a grating of 1800 lines/mm. The slit function has been measured using Cd and Hg spectral lamps and the tunable laser system PLACOS [Nevas et al., 2014] and was found very similar to Gaussian with a full width at half maximum (FWHM) of about 0.25nm for Phaethon #1 and ~0.4nm for Phaethon #2 and #3. The CCD detector is a Sony 2048-pixel linear array with Deep UV coating that enhances its response below 350nm and is thermoelectrically cooled to 5°C. The entrance optics comprises a telescope with a planoconvex lens which focusses the collected radiation onto one end of an optical fiber, with a field of view of about 1.5°. Neutral-density optical filters, cut-off filters and transmission diffuser plates, alone or in various combinations are placed on a filter wheel with 8 positions. One position is clear for scattered radiation measurements and one is opaque for dark-signal measurements. The collected light is transferred through a fused silica UV/Vis optical fiber with high OH and a numerical aperture of 0.22 to the spectrograph entrance slit. The entrance optics is mounted on a 2-axes tracker with pointing resolution of 0.125°, allowing accurate tracking for both direct-sun and sky-radiance measurements at different elevation and azimuth angles. The operating software controls the positioning of the tracker and filter wheel, as well as the data acquisition.

2.2 Ground-based measurements

In the framework of the "Optimization and expansion of ground infrastructure for the validation of satellite-derived column densities of atmospheric species" (AVANTI) project, a short campaign was organized to investigate the spatial variability of tropospheric columns of air pollutants in the greater area of Thessaloniki and the effect of this variability on the comparisons of satellite with ground based data. In addition to the Phaethon system that operates regularly at the roof of the Physics Department in the Aristotle University campus which is located in the center of Thessaloniki with prevailing urban conditions (UC), two identical systems have been deployed at two different locations within an area of about 13 km by 26 km (see Fig. 1). At the exact same locations another campaign has taken place in 2006 to investigate the spatial variability of aerosol optical depth and UV irradiance within an area comparable to the OMI pixel footprint [Kazadzis et al., 2009]. These three locations are characterized by diverse local atmospheric pollution patterns representing urban, suburban and rural conditions. Phaethon #2 was installed at a site with rural conditions (RC) near the sea shore about 26 km south of Thessaloniki city center, where it has been operating from November 1st 2014 through January 31st 2015. Phaethon #3 was installed at the Alexander Technological Educational Institute of Thessaloniki (ATEITH) located in an area with sub-urban conditions (SC) ~13 km north-west of Thessaloniki center and it has been operating there from January 20th to May 11th 2015. Unfortunately, due to a technical problem in one of the spectrometers only a short period of parallel measurements is available at all three locations.

During the campaign the MAX-DOAS systems were performing both direct-sun and scattered light measurements. A sequence of sky radiance measurements included the zenith direction and the off axis elevation angles 2º, 3º, 4º, 5º, 8º, 10º, 12º, 15º, 30º and 45º. These sequences were performed at a fixed azimuth angle of 255º, a direction free of significant obstacles and at azimuth angles of 80º relative to the solar azimuth. For this study we used observations at all available azimuth angles, but only at the elevation angles of 15º and 30º in order to avoid uncertainties introduced due to aerosol loadings at lower elevation angles.

The measured sky radiance spectra were analyzed by means of the QDOAS v2.109_3 software developed by the Royal Belgian Institute for Space Aeronomy (BIRA-IASB) and S[&]T (https://www.stcorp.nl/) [Danckaert et al., 2015]. For the DOAS analysis the fitting window 400-450nm was used. A polynomial of order 4, an offset of second order and a Ring effect spectrum, calculated according to the approach described by Chance and Spurr [1997], were also included in the DOAS analysis. Along with the NO_2 cross section at 298K [Vandaele et al., 1998], the cross sections of O_3 at 223K [Bogumil et al., 2003], O_4 at 296K [Greenblatt et al., 1990] and H_2O (HITRAN database, https://www.cfa.harvard.edu/hitran/) were also taken into account. Fig. 2 presents an example of NO_2 slant column fitting for an elevation angle of 5º obtained for the UC site on 6 November 2014, around 10:30 UTC (SZA about 57º). For the retrieval of tropospheric NO_2 the zenith spectrum of each sequence of elevation angles was used as reference in order to minimize the influence of the stratospheric component in the calculated off-axis differential Slant Column Densities (dSCDs) [Hoenninger et al, 2004]. The tropospheric vertical column density (VCD) can be calculated for each elevation angle by the formula suggested in Ma et al. [2013]:

$$VCD_{trop} = \frac{dSCD_{trop}}{dAMF_{trop}} \quad (1)$$

where $dAMF_{trop}$ is the tropospheric differential air-mass factor which represents the absorption enhancement in the effective light path caused by the combination of single and multiple scattering and absorption processes.

Tropospheric NO_2 AMFs were calculated by means of the modelling package libRadtran version 1.7 [Mayer and Kylling, 2005] using a pseudo-spherical discrete ordinate radiative transfer method [Buras et al, 2011]. For the simulations typical values of aerosol single scattering albedo (0.95), aerosol asymmetry factor (0.7) and surface albedo (0.1) were assumed [Bais et al., 2005; Kazantzidis et al., 2006]. A key parameter affecting significantly the radiative transfer simulations and therefore the calculation of AMFs is the trace gas vertical distribution in the atmosphere. In this study, mean vertical profiles from the air quality modelling tool consisting of the photochemical grid model CAMx and the mesoscale weather prediction system WRF were used. The description of this modelling tool and details about the simulations are presented in the next section. For the AMF simulations the mean vertical profile of the aerosol optical depth (AOD) at 355 nm calculated from observations of the LIDAR system operating in LAP/AUTH during the period 2001-2007 [Giannakaki et al., 2010] was used for all three locations. According to Kazadzis et al. [2009] the spatial variability in AOD loading and AOD profile between the three locations is very small. The average AOD differences of the RC and the SC sites from the UC site were found to be 0.07 and 0.01, respectively. The LIDAR profile was scaled using different total AOD values in the range 0-1.5.

AMF look up tables (LUTs) were constructed from the radiative transfer simulations for each measurement location. Along with the AOD, other variables of these LUTs are the solar zenith angle, the elevation viewing angle and the azimuth angle relative to the solar azimuth. An example of the AMFs calculated at elevation angles 15° and 30° versus AOD for each location is presented in Fig. 3. The AMF corresponding to each measurement is calculated by multi-linear interpolation, using AOD measurements from the CIMEL sun-photometer operating at Thessaloniki (http://aeronet.gsfc.nasa.gov/).

Prior to their deployment at the campaign sites, the three systems were operating for a few days in parallel in the University campus and their inter-comparison tests revealed a very good agreement and no systematic differences (Fig. 4, Table 2). Tropospheric NO_2 measurements performed within 10 minutes were included in the inter-comparison.

2.3 Satellite observations

For each of the campaign locations an overpass data set was extracted from OMI, GOME2A and GOME2B observations. Details of this data selection are discussed in Sect. 3.2.

The Ozone Monitoring Instrument (OMI) is one of four instruments on board the NASA EOS-Aura spacecraft, launched on 15 July 2004 in a sun-synchronous ascending near-polar orbit with around 1:45 pm local equator crossing time [Levelt et al., 2006]. OMI is a compact nadir viewing, wide swath (of 2600 km that permits a near daily global coverage), ultraviolet-visible (270 nm to 500 nm) imaging spectrometer that was contributed to the Aura mission by the Netherlands and Finland. The foot pixel size of OMI at nadir is 13 km x 24 km, degrading towards swath edges [Curci et al., 2010]. The operational total and tropospheric NO_2 columns from OMI are generated by NASA and distributed by the Aura Validation Data Center (AVDC) (http://avdc.gsfc.nasa.gov).

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The Global Ozone Monitoring Experiment-2 (GOME-2) instrument is a nadir-viewing scanning spectrometer that samples the 240–790 nm spectral range with a spectral resolution between 0.24–0.5 nm, with an across-track scan time of 6 seconds and a default swath width of 1920 km [Callies et al., 2000]. GOME-2 ground pixels have a footprint size of 80 km x 40 km. Currently there are two GOME-2 instruments operating, one on board EUMETSAT's Meteorological Operational Satellite -A (MetOp-A), launched in October 2006, and the other mounted on the MetOp-B satellite, launched in September 2012. MetOp-A and MetOp-B are flying on a sun-synchronous orbit with an equator crossing time of 09:30 local time (descending node) and a repeat cycle of 29 days. Global coverage of the sunlit part of the atmosphere can be achieved almost within 1.5 days.

The operational GOME-2 total and tropospheric NO_2 columns from MetOp-A and MetOp-B are generated at the German Aerospace Center (DLR) using the UPAS (Universal Processor for UV/VIS Atmospheric Spectrometers) environment version 1.3.9, implementing the level-1-to-2 GDP 4.7 algorithm (http://atmos.eoc.dlr.de/gome2/). The data processing is commissioned by EUMETSAT within the auspices of the Satellite Application Facility for Atmospheric composition and UV radiation, O3MSAF, project.

2.4 Air quality modelling tool

The comparison of satellite-derived tropospheric NO_2 with ground-based observations in areas with inhomogeneous distribution of air pollution is usually poor, due to the different geometries associated with the measurement methods of the two datasets [Celarier et al., 2008; Kramer et al., 2008; Irie et al., 2012]. Ground-based measurements are representative of the absorption of radiation in a particular viewing direction and path, while measurements of satellite sensors are sensitive to absorption of radiances emerging from a wide area determined by the size of the satellite pixel. In order to overcome this problem and improve the comparisons in the greater area of Thessaloniki, the satellite data are adjusted using factors derived from air quality simulations.

The modeling system employed for the calculation of the adjustment factors consisted of the Comprehensive Air Quality Model with Extensions (CAMx, version 5.3) [ENVIRON, 2010] off-line coupled with the Weather Research and Forecasting - Advanced Research Weather (WRF - ARW, version 3.5.1) [Skamarock et al., 2008]. The model simulations were performed for the period November 2014 – May 2015.

The WRF - ARW is a next-generation mesoscale Numerical Weather Prediction (NWP) model [Kalnay E., 2003] designed to serve both atmospheric research needs and operational weather forecasting. WRF simulations were carried out over two domains in Lambert Conic Conformal projection; a 6 km resolution coarse domain (d01, mesh size of 343x273) that covers the greater area of Balkan Peninsula and a nested (two-way nesting) domain (d02) that focuses over the area of Thessaloniki with a higher spatial resolution of 2 km (mesh size of 60x60). The domains' vertical profile extends up to 16 km above ground level and contains 28 layers of varying thickness with higher resolution near the ground. The initial and boundary meteorological conditions were taken from the European Centre for Medium – Range Weather Forecast, ECMWF, in spatial resolution of 0.125°x0.125° (~12.5 km) and temporal resolution of 6 h. Microphysical processes were parameterized using the New Thompson et al. [2008] scheme, whereas convection in the coarse domain (d01) was parameterized with the Grell-

Devenyi (GD) ensemble scheme [Grell and Devenyi, 2002]. For the innermost domain (d02), no convective parameterization was used. Radiative transfer processes were handled with the shortwave and longwave RRTMG schemes [Iacono et al., 2008]. The surface layer was parameterized using the Eta similarity scheme [Janjic, 2002], while for the planetary boundary layer the Mellor-Yamada-Janjic parameterization scheme [Janjic and Zavisa, 1994] was used. Finally, for the parameterization of land surface processes the Noah Land Surface Model [Tewari, et al., 2004] was applied.

CAMx is a 3D Eulerian photochemical dispersion model widely used in air quality studies during the last decade [Liora et al., 2016; Poukou et al., 2014; Kukkonen et al., 2012; Lee et al., 2009; Lei et al., 2007] several of which are related to joint analysis of simulated and remotely sensed pollutant concentration data [Zyrichidou et al 2009; 2013; 2015; Zyryanov et al 2012; Huijnen et al 2010]. In the current study, the simulation domains of CAMx were identical, in terms of horizontal spatial resolution and projection, with those of the WRF model in order to avoid errors introduced by interpolations between grids, but were slightly less spatially extended (337 x 267 cells for the Balkan domain and 56 x 56 cells for the Thessaloniki domain). CAMx grids were structured in 22 vertical layers extending up to 10 km above ground level. The gaseous and particulate matter anthropogenic emissions for the Balkan domain were derived from the European scale emission database of The Netherlands Organisation (TNO) for the reference year 2007 [Kuenen et al., 2011]. For the greater area of Thessaloniki, the anthropogenic emissions were calculated using mainly the methodologies and emission factors of the EMEP/CORINAIR emission inventory guidebook [EEA, 2006]. More specifically, the anthropogenic emission model MOSESS (Model for the Spatial and Temporal Distribution of Emissions) [Markakis et al., 2013] was applied for the calculation of CO, NOx, SO_2, NH_3, NMVOC, PM10 and PM2.5 emissions as well as for their chemical, spatial and temporal analysis. The NOx emissions for the domain of Thessaloniki during the period of the campaign are presented in the upper panel of Fig. 5. Particulate matter emissions from natural sources (windblown dust, sea salt) as well as biogenic volatile organic compounds from vegetation were estimated using the Natural Emissions model (NEMO) [Poupkou et al., 2010; Liora et al., 2015; Liora et al., 2016]. The gas-phase chemical mechanism employed in CAMx was the 2005 version of Carbon Bond (CB05) [Yarwood et al., 2005]. The chemical boundary conditions for CAMx runs were taken from the global model system C-IFS-TM5 results, available in the framework of the EU project MACC-III.

The adjustment factors of the satellite data were calculated by the following procedure: For each 2 km x 2 km grid cell included in a typical OMI pixel size area at nadir (7 x 13 cells), centered at the location of each monitoring site, the tropospheric NO_2 VCD was derived by integrating vertically the model-derived hourly mean mixing ratios of NO_2. The lower panel in Fig. 5 presents the simulated NO_2 VCD averaged over the period of the campaign for each cell within the OMI footprint over the three campaign sites. Then the tropospheric NO_2 VCD for the grid cell that contains the coordinates of each monitoring site was divided by the VCD averaged over the OMI pixel area.. Finally, the OMI data were multiplied by these adjustment factors in order to minimize the effect of the differences in the spatial distribution of NO_2 and achieve better agreement with the ground-based observations, which are assumed to represent mostly the VCD above the grid cell where they are located. It should be mentioned here that the method was applied only to OMI data because for GOME-2 the sub-satellite pixel is very large, covering typically the entire domain of Fig. 1. A similar method has been previously employed on comparisons of

GOME2A tropospheric NO_2 observations with ground-based data over the Observatoire de Haute Provence (OHP) at southern France [Lambert et al., 2011], leading to a slight improvement of the correlation coefficient from 0.63 to 0.71 and the slope of the linear regression from 0.69 to 0.73.

3 Results and discussion

3.1 NO_2 tropospheric columns in the greater area of Thessaloniki

The hourly mean tropospheric NO_2 measurements obtained by Phaethon at the three campaign sites are presented in Fig. 6. The NO_2 at the city center of Thessaloniki (UC) in blue circles are much higher than at the SC (red circles) and RC (yellow circles) sites, especially during winter months. The averaged measured tropospheric NO_2 over the campaign period is ~11.83±7.06 x 10^{15} molecules cm^{-2} for the center of Thessaloniki, whereas the average for the SC and RC sites is 5.80±3.53 x 10^{15} and 4.64±2.24 x 10^{15} molecules cm^{-2}, respectively. The average tropospheric NO_2 at SC and RC sites are in general comparable. However, some positive excursions are observed at SC because this site is likely affected by NO_2 transported from urban areas or by local pollution sources depending on weather conditions. The SC site is adjacent to the city center and to Thessaloniki's industrial area, although industrial activity has been drastically reduced over the last five years. Negative values of the VCD obtained from measurements at higher elevation angles, such those used in this study (15° and 30°), indicate that the NO_2 absorption of the Fraunhofer reference spectrum is underestimated and cannot be assumed negligible compared to the analyzed spectra.

3.2 Comparison of ground-based tropospheric NO_2 with OMI, GOME-2/MetOp-A and GOME-2/MetOp-B observations

For each of the three campaign sites ground-based measurements of tropospheric NO_2 (both 15° and 30° were used) are compared with products from satellite overpass data, as discussed in Section 2.2. The collocation criteria used are the solar zenith angle (SZA), the cloud fraction (CLF) and the temporal and spatial difference of the measurements. More specifically, only satellite data corresponding to SZA ≤ 75° and CLF ≤ 20% (corresponds to observations with a radiance reflectance of less than 50% from clouds [van der A et al., 2008]) were selected and averages of Phaethon measurements within ±30 min around the overpass time were included in the comparison. Moreover, only OMI pixels that are not affected by the OMI row anomalies [see OMI Data User's Guide, 2012] were used in this study in order to obtain good quality and meaningful data. Finally, the upper limit for the distance between the measurement site and the center of the sub-satellite pixel was set to 25 km for OMI and 50 km for GOME-2 sensors, in correspondence to their typical pixel sizes.

Scatter plots of tropospheric NO_2 data for each campaign site and satellite sensor separately are presented in Fig. 7, while averages and statistics of the comparisons are shown respectively in Tables 3 ad 4. The satellite instruments seem to underestimate significantly the NO_2 levels over the urban area of Thessaloniki (right column in Fig. 7, Table 3 and Table 4). This finding might be ascribed to the fact that the satellite-derived columns represent the average pollution loading in the sub-satellite pixel area, while ground-based data are mostly representative of the NO_2 amounts in air masses above and in close proximity to the monitoring site. In the case of Thessaloniki, the significant contribution of lower pollution levels in the suburbs results into lower estimates of NO_2 by the satellite. Several studies have reported significant differences in air pollution between the city center and the suburbs using long-term observations by the air quality monitoring network of Central Macedonia [Poupkou et al., 2011; Moussiopoulos et al., 2008]. The fact that OMI observations compare better with the ground-based NO_2 data can be attributed mainly to its smaller pixel size and to its higher sensitivity in the boundary layer compared to GOME-2. The OMI sensor provides better detection of higher local pollution levels [Kramer et al., 2008], due to its higher spatial resolution (13 x 24 km^2 at nadir), compared to GOME-2 sensors which detect the average NO_2 concentration over a larger area (80 x 40 km^2). Moreover, OMI passes over Thessaloniki at around local solar noon (~10:30 UT), when tropospheric NO_2 levels are normally reduced due to photochemical processes [Crutzen, 1979]. On the contrary, GOME2A and GOME2B satellites pass over Thessaloniki during morning hours (between 7:30 - 9:00 UT), when local NO_2 concentrations in the city center are usually much higher.

Ground-based and satellite-derived NO_2 tropospheric VCDs are in better agreement over the rural (RC) and sub-urban (SC) stations (left and middle columns respectively in Fig. 7, Table 3 and Table 4). However, there is poor correlation between Phaethon and GOME-2 sensors over those two locations (Table 4) probably due to the limited number of data pairs and some elevated NO_2 concentrations observed by the Phaethon system over the SC location which are not detected by GOME-2 sensors.

3.3 Reconstruction of OMI observations

Hourly data of tropospheric NO_2 derived from the CAMx simulations according to the method described in section 2.4 are presented for each campaign location separately in Fig. 8 (left panels), averaged over the OMI nadir pixel and for the grid point of 2x2 km^2 corresponding to each ground-based site. Adjustment factors, i.e. ratios of these simulations, are also shown in Fig. 7 (right panels, grey lines) for all hourly data in each day. As expected, the adjustment factor is variable during each day with increasing variability from the RC to the UC sites. Adjustment factors corresponding to the OMI overpass time, which were used for the reconstruction of the satellite dataset, are presented with colored lines. For the center of Thessaloniki (UC) the mean estimated ratio is 2.20 ± 0.75 (right column in Table 5). Relatively higher values are observed during spring (2.39 ± 0.80) and smaller during the winter months (2.03 ± 0.64). In the other two locations of the campaign the adjustment ratio is much smaller. In the case of the RC site (left column in Table 5), the ratio is on average close to unit (0.96 ± 0.18). This indicates that the area within the OMI nadir pixel size corresponds mostly to lower NO_2 levels, same as the Phaethon monitoring site. On the other hand, the majority of the ratios calculated for the SC location (middle row in Fig. 7) are slightly lower than 1, leading to an average of 0.78 ± 0.24, which indicates higher average NO_2 concentrations over the OMI footprint than at the ground-based monitoring site. These results can be ascribed to the fact that the SC station is located about 13 km west of the center of Thessaloniki, hence, the sub-satellite pixel area can be affected by heavy pollution levels observed in the city center. However, ratios larger than unit are observed occasionally (~11% of all simulations), possibly related to local pollution sources or to NO_2 transportation by the prevailing winds from neighboring locations.

The comparison between ground-based and OMI observations over the campaign locations before and after the satellite data adjustment is presented in Fig. 9. Over the UC monitoring site Phaethon compares better with the adjusted OMI data. The OMI average underestimation has changed from 6.03±6.04 x 10^{15} to 1.15±6.32 x 10^{15} molecules cm^{-2} and the slope of the fitted least squares regression line has been improved from ~0.2 to ~0.4. The OMI data over the other two campaign stations have not been significantly affected by the adjustment, due to better spatial homogeneity of the NO_2 loading. It should be noted here that the calculation of the adjustment factors assumed that the OMI pixel is centered at the monitoring site and its size is always equal to the typical nadir pixel. In reality, these assumptions are not always valid [de Graaf et al., 2016], therefore the method of deriving adjustment factors is associated with some uncertainty which increases with pixel size and distance of its center from the ground-based monitoring system. The use of actual satellite geometry for each day is complex and would require a much larger domain for the air-quality simulations, more than double the currently used (120x120 km^2) in order to include all possible pixel sizes and positions for each location. However, such simulations were not available for this study.

Additional uncertainties may arise from the vertical integration of the air-quality simulations to derive vertical column of NO_2 representative for the troposphere and the assumption that it is comparable to the VCD derived by the MAX-DOAS measurements. The two methods are based on different concepts, and for the MAX-DOAS it is not possible to define a top level for the tropospheric NO_2 column which could be used to integrate vertically the model simulations. The importance of this effect was investigated in a sensitivity analysis which showed that the uncertainty in the calculation of the VCD of NO_2 associated with the upper level used in the vertical integration of the model derived mixing ratio is less than 1% for different upper levels between 6 and 9 km.

4 Summary and conclusions

An experimental campaign took place in the greater Thessaloniki area, Greece, within the period November 2014 – May 2015, with the aim to investigate the impact of different spatial sampling of ground-based and space borne measurements on tropospheric NO_2 column density. In this study, tropospheric NO_2 derived by Phaethon ground-based DOAS/MAX-DOAS systems at three different locations characterized by diverse pollution loadings were presented and compared with corresponding satellite products from OMI/Aura and GOME-2/MetOp-A and /MetOp-B. The agreement of Phaethon measurements with satellite columns over the rural area is good for all three instruments, although the variability is higher for GOME2B. A strong positive bias in ground-based NO_2 columns is found over the urban area. This is attributed to the great inhomogeneity of NO_2 concentrations over the area covered by the city of Thessaloniki. A significant portion of the area surrounding the city center and included in a typical sub-satellite pixel corresponds mostly to rural atmospheric conditions. Therefore the average tropospheric NO_2 is significantly reduced compared to Phaethon data that probe air masses over the urban center of the city.

The agreement of Phaethon data with OMI retrievals is better compared to GOME-2 sensors, due to its smaller pixel footprint. For GOME2A and GOME2B the city center is a very small portion compared to the entire area covered by the satellite pixel size, thus the contribution of the increased NO_2 loadings to the average column density is very weak.

The application of adjustment factors on OMI data derived from NO_2 simulations with an air quality modelling tool reduced the effect of spatial differences between OMI and Phaethon observations. The improvement in the comparisons is more evident for the urban site, where the mean difference between OMI and Phaethon were reduced from -6.03 x 10^{15} to -1.15 x 10^{15} molecules cm^{-2}. The effect on the rural and suburban locations is negligible, due to the reduced spatial inhomogeneity of the air-pollution.

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Table 1. Information on campaign locations and measurements performed there.

	LAP-AUTH (UC)	ATEITH (SC)	Epanomi (RC)
Air quality conditions	Urban	Sub-urban/Industrial	Rural
Latitude	40.63N	40.65N	40.37N
Longitude	22.96E	22.81E	22.98E
System	Phaethon #1	Phaethon #3	Phaethon #2
Period of operation	1/11/2014 - 11/5/2015	20/1/2015 - 11/5/2015	1/11/2014 - 31/1/2015
Number of NO_2 trop. VCD measurements	7930	16716	5738

Table 2. Statistics from the comparison of Phaethon #2 and #3 systems to Phaethon #1 during the period 11 - 18 October 2014.

	Phaethon #2	Phaethon #3
Number of observations	75	75
Correlation coefficient (r)	0.95	0.92
Slope of the linear fit	1.03	1.07
Mean bias [x10^{15} molec. cm^{-2}]	0.58	0.73
Standard deviation (1σ) [x10^{15} molec. cm^{-2}]	2.51	3.12

Table 3. Average and standard deviation of space-borne and ground-based tropospheric NO_2 observations over each campaign location. Phaethon mean values have been calculated from measurements within ±30 min around the satellite overpass time.

NO_2 trop. VCD mean ($\pm1\sigma$) [x10^{15} molec. cm^{-2}] from	RC site	SC site	UC site
OMI	4.21 (± 1.86)	2.91 (± 1.54)	3.78 (± 2.28)
Phaethon (OMI overpass time)	4.19 (± 2.43)	2.67 (± 1.31)	9.81 (± 7.04)
GOME2A	3.04 (± 1.58)	2.17 (± 1.25)	2.90 (± 1.48)
Phaethon (GOME2A overpass time)	4.05 (± 1.67)	4.42 (± 2.88)	12.02 (± 7.66)
GOME2B	3.33 (± 2.50)	2.35 (± 1.19)	2.87 (± 1.75)
Phaethon (GOME2B overpass time)	5.45 (± 2.25)	4.41 (± 2.78)	12.45 (± 8.42)

Table 4. Statistics from the comparison of space-borne and ground-based NO_2 tropospheric VCDs for each campaign location.

	Compared to Phaethon NO_2 trop. VCD	RC site	SC site	UC site
OMI	Number of collocations	17	28	32
	Correlation coefficient (r)	0.45	0.46	0.57
	Mean bias [$x10^{15}$ molec. cm^{-2}]	0.02	0.24	-6.03
	Standard deviation (1σ) [$x10^{15}$ molec. cm^{-2}]	2.31	1.50	6.04
GOME2A	Number of collocations	22	34	39
	Correlation coefficient (r)	0.40	0.03	0.31
	Mean bias [$x10^{15}$ molec/cm^2]	-1.00	-2.25	-9.12
	Standard deviation (1σ) [$x10^{15}$ molec. cm^{-2}]	1.78	3.11	7.33
GOME2B	Number of collocations	27	52	55
	Correlation coefficient (r)	-0.09	-0.07	0.22
	Mean bias [$x10^{15}$ molec/cm^2]	-2.12	-2.07	-9.58
	Standard deviation (1σ) [$x10^{15}$ molec. cm^{-2}]	3.51	3.09	8.21

Table 5. Average and standard deviation of the CAMx simulated NO_2 tropospheric VCDs for each campaign location during the entire period of the campaign, for the grid of each site (2x2 km^2) and for the OMI nadir pixel size (14x26 km^2). The ratios estimated using only the NO_2 columns corresponding to the OMI overpass time have been used as adjustment factors for the reconstruction of the OMI observations.

Mean (±1σ) NO_2 trop. VCDs [$x10^{15}$ molec. cm^{-2}] and adjustment factors from		RC site	SC site	UC site
All simulations	2x2 km^2	3.70 (± 2.74)	5.02 (± 3.73)	11.58 (± 8.43)
	14x26 km^2	3.59 (± 2.37)	5.73 (± 3.22)	5.87 (± 3.36)
	Ratio	1.00 (± 0.16)	0.85 (± 0.25)	1.91 (± 0.75)
Simulations near OMI overpass time	2x2 km^2	2.85 (± 1.97)	3.62 (± 2.64)	12.43 (± 8.66)
	14x26 km^2	2.85 (± 1.55)	4.50 (± 2.36)	5.46 (± 3.12)
	Ratio	0.96 (± 0.18)	0.78 (± 0.24)	2.20 (± 0.75)

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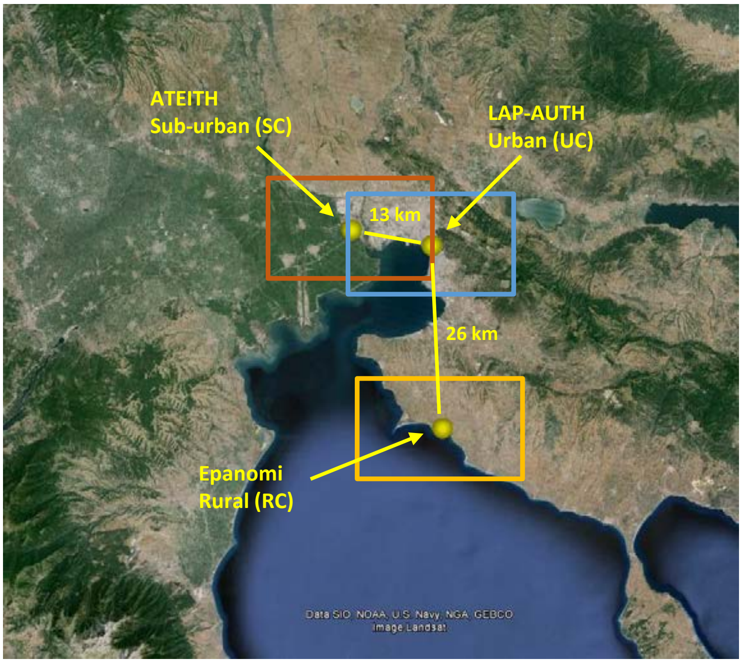

Figure 1: Map of the greater Thessaloniki area with the three sites of measurements: UC (blue), SC (red) and RC (yellow). The rectangular outlines represent the area covered by the nadir pixel size of OMI centered at each location (Courtesy of Google Earth NASA Images).

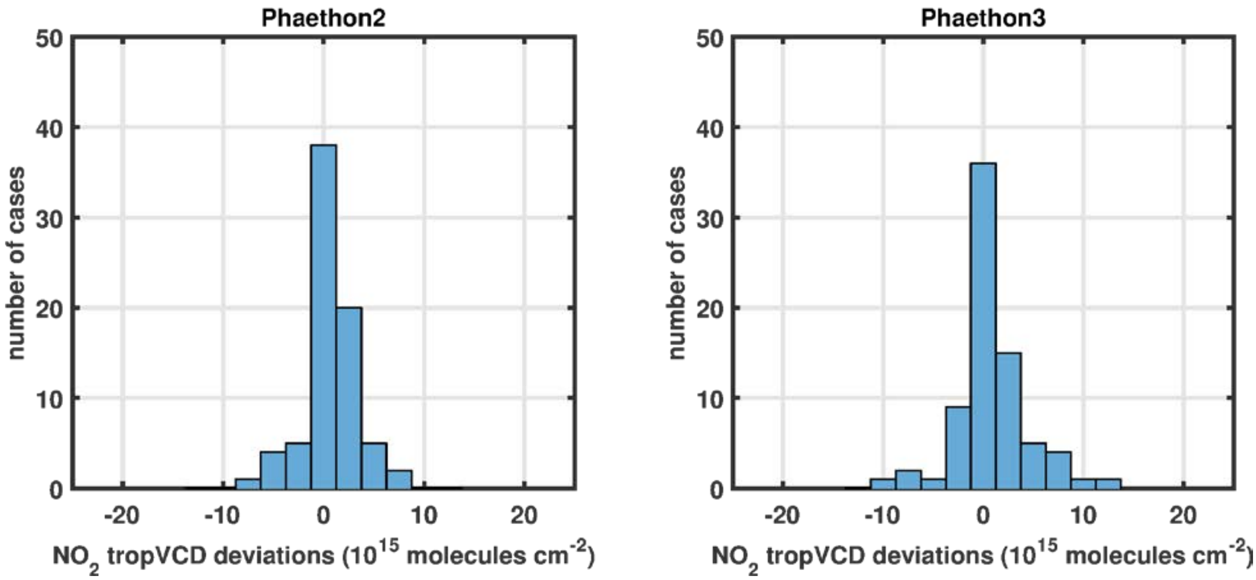

Figure 2: Histograms of the NO_2 tropospheric VCD differences of Phaethon #2 and #3 relative to Phaethon #1. The three systems were operating in parallel in the University Campus for 8 days, from 11 to 18 October 2014.

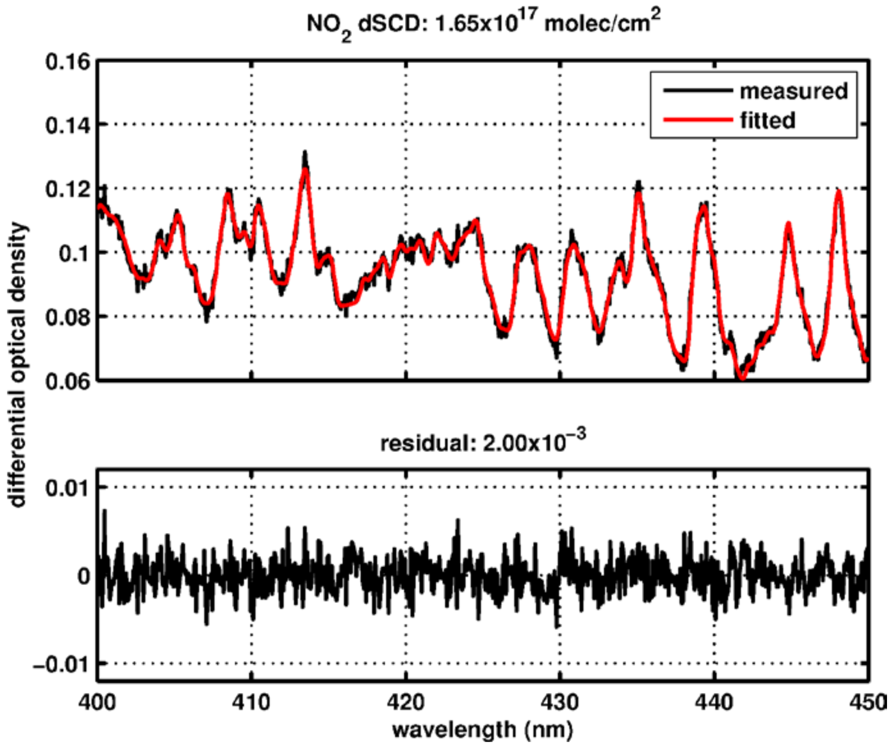

Figure 3: Example of NO_2 fitting results obtained at the UC site on 6 November 2014, around 10:30 UTC, at an elevation angle of 5° and a SZA ~57°. The upper panel shows the measured (black) and the fitted (red) NO_2, and the lower panel shows the residual of the DOAS fit.

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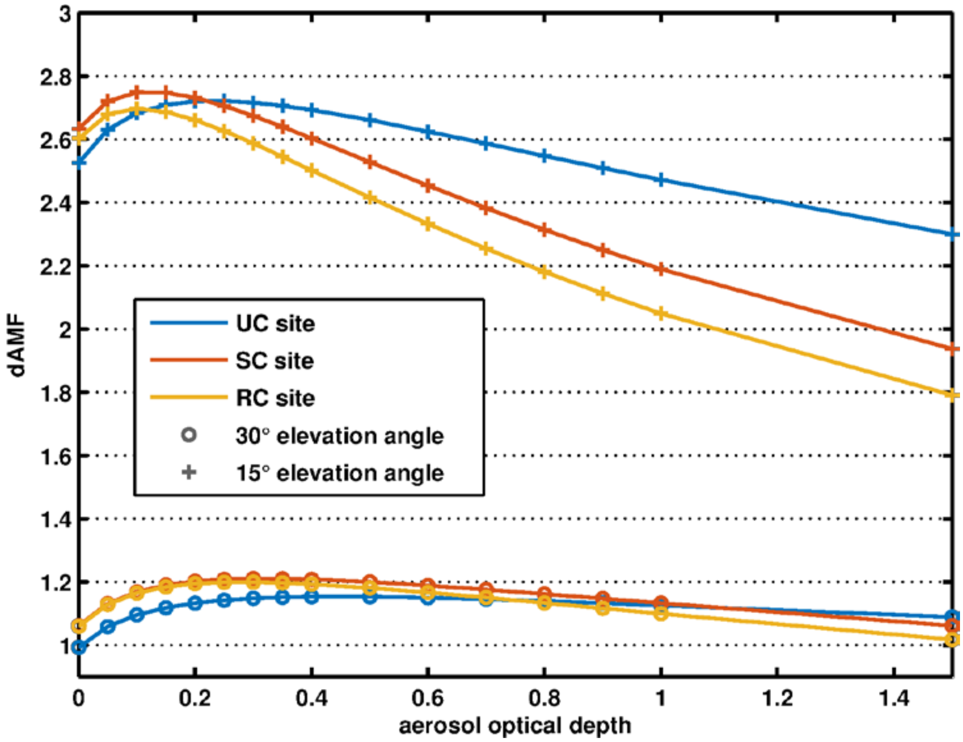

Figure 4: Example of the AMFs calculated with libRadtran at SZA 40º and azimuth angle 100º relative to the sun for each campaign site. The AMFs at 15º (crosses) and 30º (circles) elevation angles are plotted versus the AOD.

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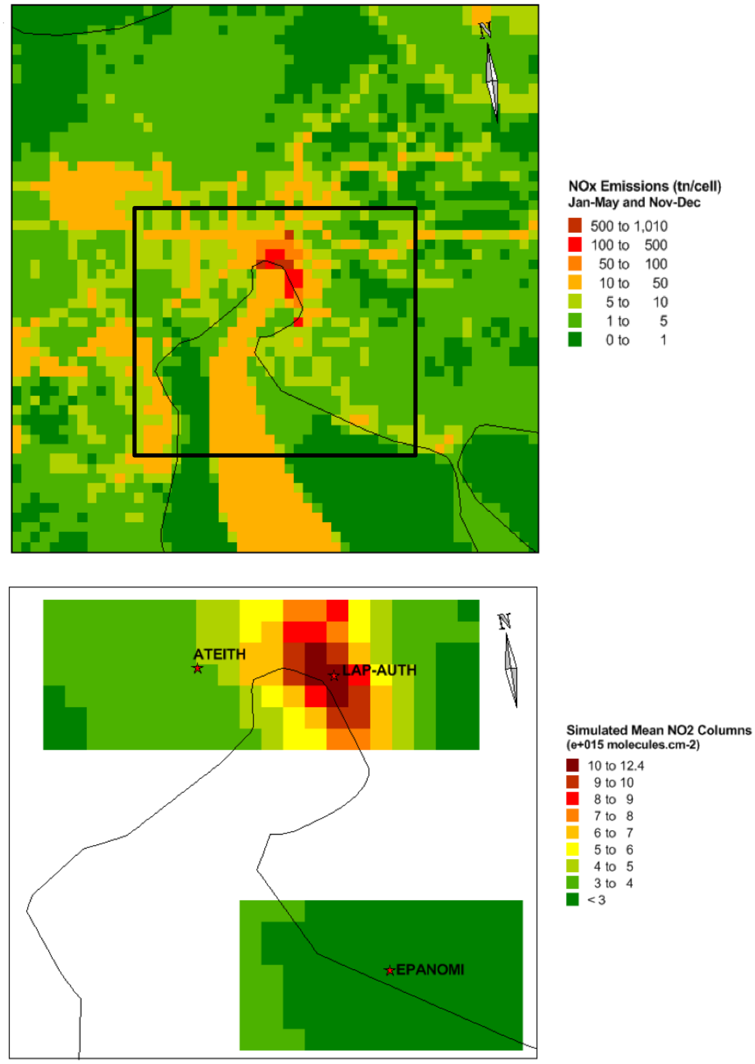

Figure 5: The upper panel shows the NOx emissions for the domain of Thessaloniki during the months included in the period of the campaign (November 2014 – May 2015). For the framed area the simulated NO_2 VCD averaged over the period of the campaign is presented for each cell within the OMI footprint over the three campaign sites (lower panel).

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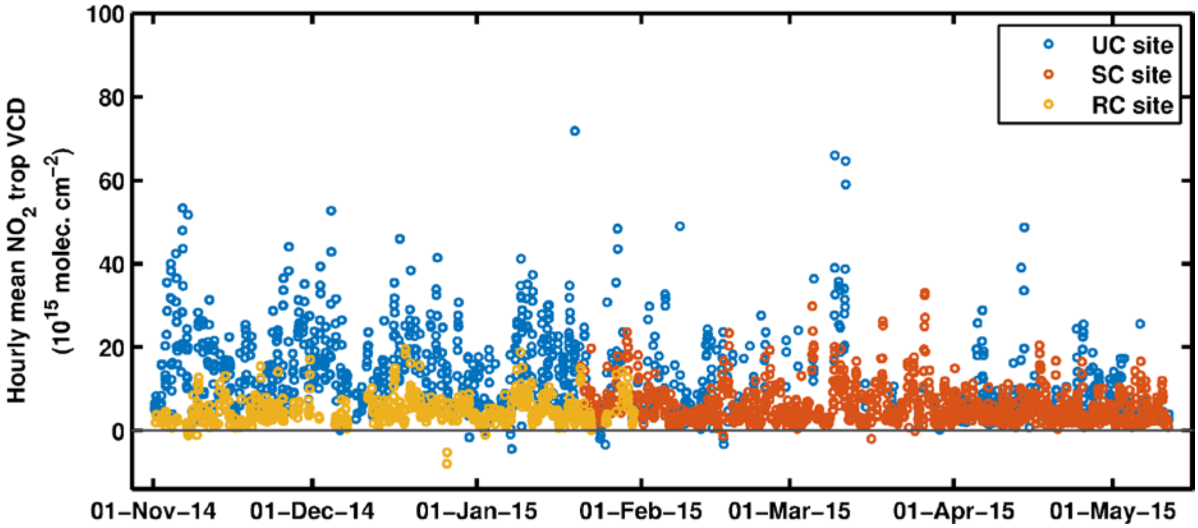

Figure 6: Time series of hourly mean tropospheric NO_2 column measurements performed by Phaethon at the three campaign sites.

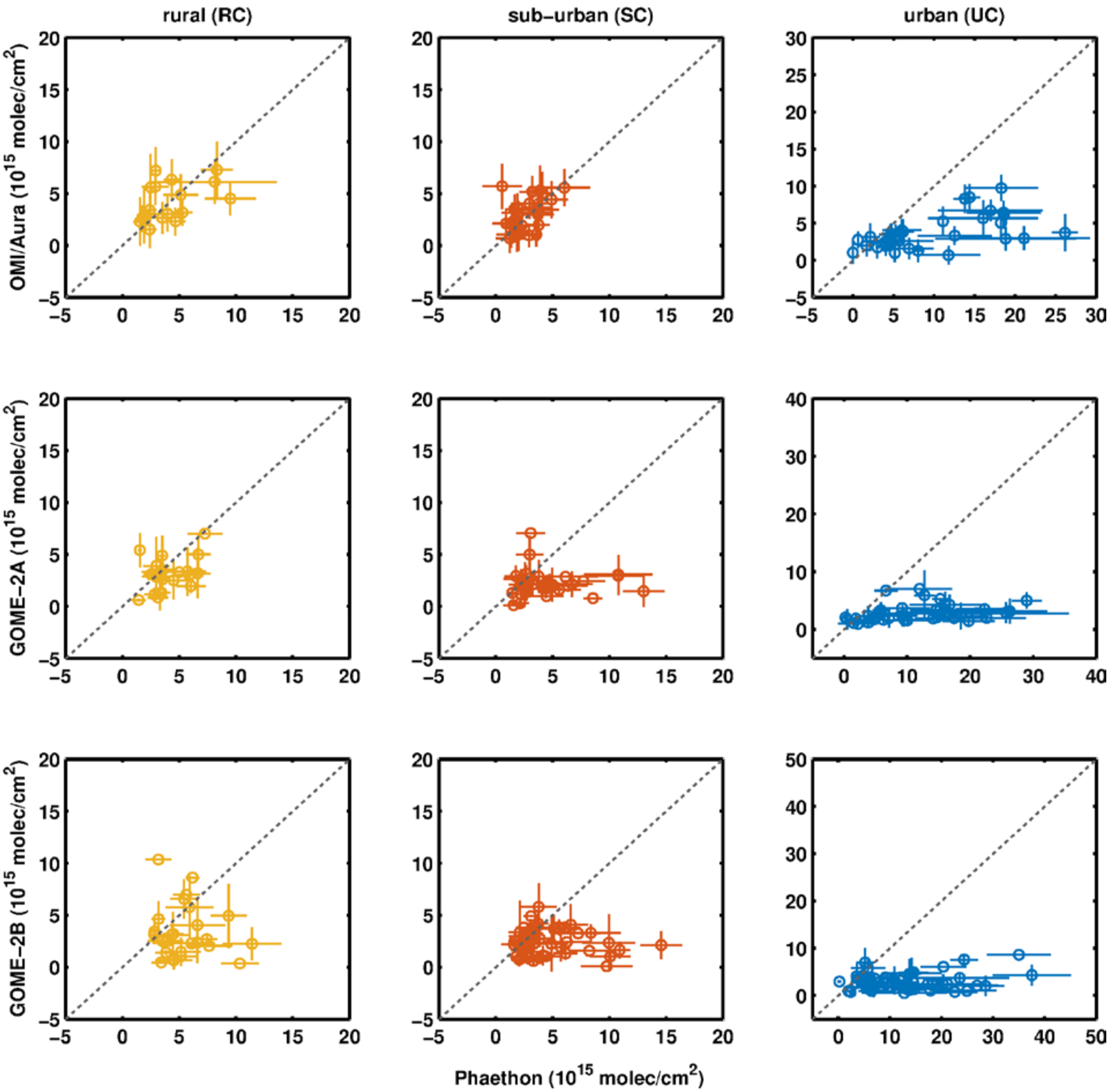

Figure 7: Scatter plots of tropospheric NO_2 derived from the ground and space for each campaign site (RC left column, SC middle column, and UC right column) and satellite sensor (OMI top row, GOME2A middle row and GOME2B bottom row). Error bars are the standard deviation of all data points entering the mean for the ground-based data and the estimated total error for the satellite overpass data. Statistics from the comparisons can be found in table 4.

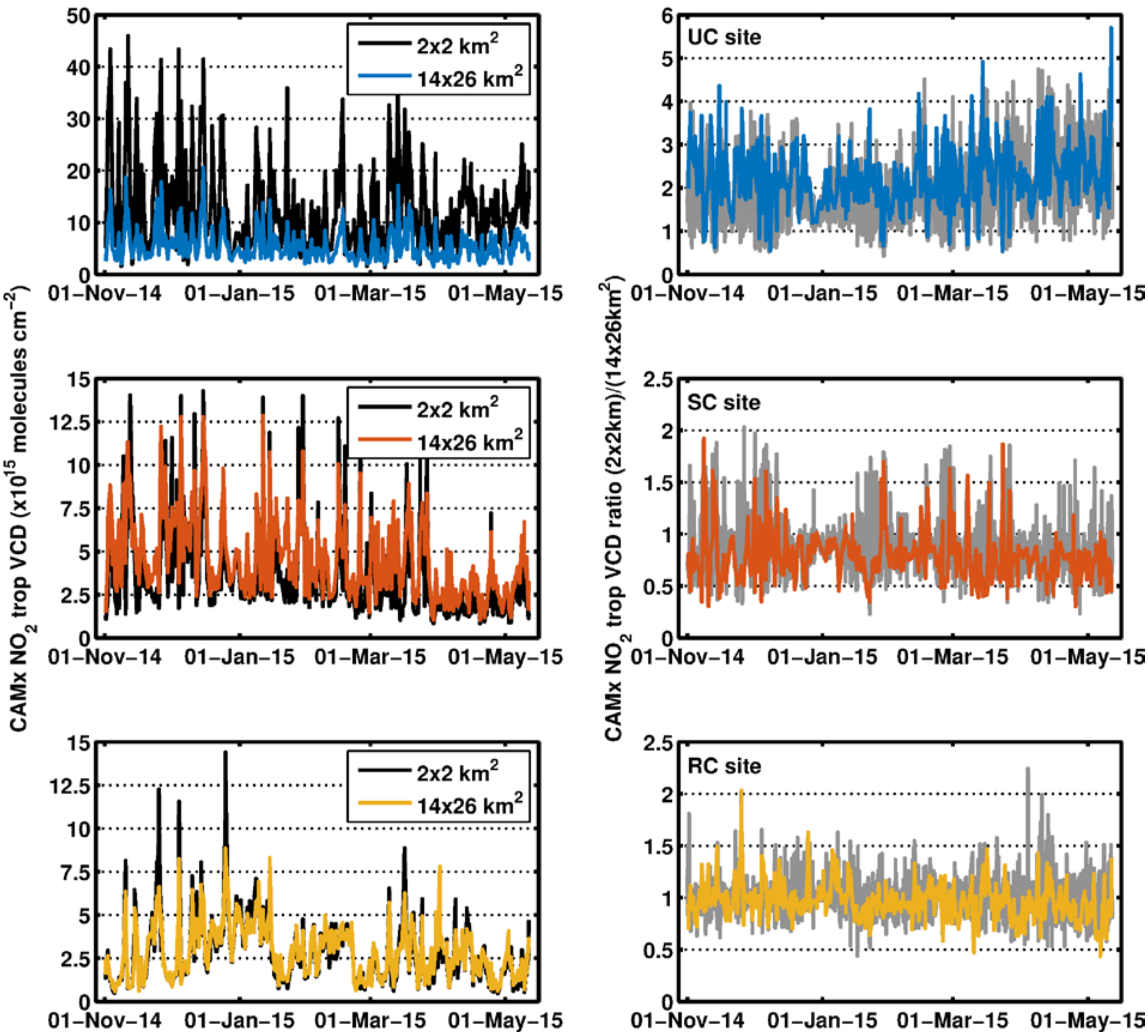

Figure 8: Hourly NO_2 tropospheric VCDs (left column) and the adjustment factors (right column) calculated by means of CAMx air quality simulations for the UC site (top row), the SC site (middle row) and the RC site (bottom row). Left panels: Only the NO_2 columns from CAMx corresponding to OMI overpass time are presented here. The black lines correspond to an area of 2x2 km^2 which includes each site and the colored lines to the OMI nadir pixel size area. Right panels: The adjustment factors (ratios) calculated using all the hourly modelled NO_2 columns are presented with grey lines while for the colored lines only simulations corresponding to OMI overpass time have been extracted.

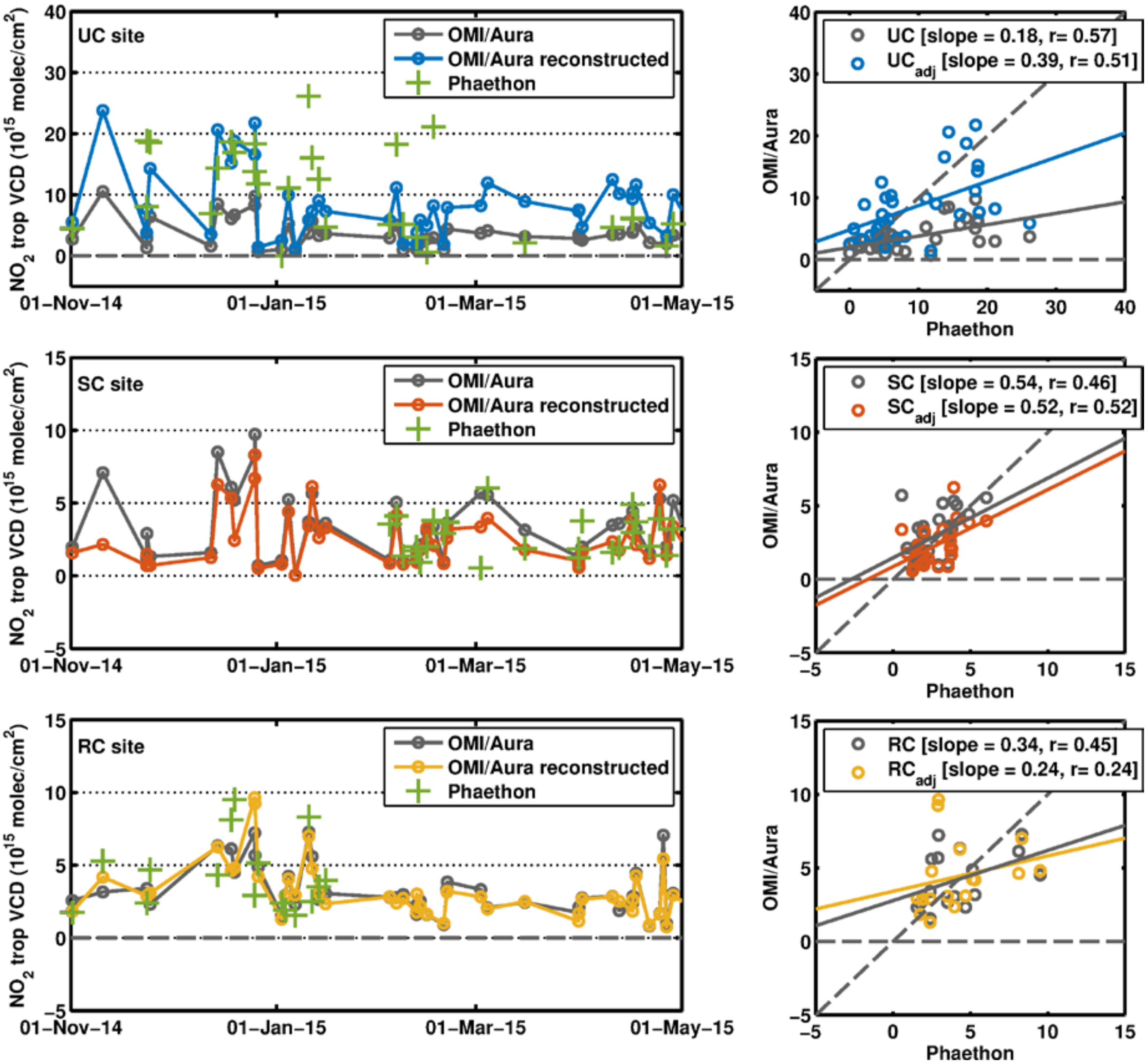

Figure 9: Time series of tropospheric NO_2 derived from Phaethon and OMI before and after the adjustment with CAMx simulations is applied (left panels). The corresponding scatter plots are shown in the right panels.