Atmos. Meas. Tech. Discuss., 8, 2437–2500, 2015 www.atmos-meas-tech-discuss.net/8/2437/2015/ doi:10.5194/amtd-8-2437-2015 © Author(s) 2015. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

New concepts for the comparison of tropospheric NO₂ column densities derived from car-MAX-DOAS observations, OMI satellite observations and the regional model CHIMERE during two MEGAPOLI campaigns in Paris 2009/10

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Received: 4 December 2014 - Accepted: 8 February 2015 - Published: 5 March 2015

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



Abstract

We compare tropospheric column densities (vertically integrated concentrations) of NO_2 from three data sets for the metropolitan area of Paris during two extensive measurement campaigns (25 days in summer 2009 and 29 days in winter 2010) within

- the European research project MEGAPOLI. The selected data sets comprise a regional chemical transport model (CHIMERE) as well as two observational data sets: ground based mobile Multi-AXis-Differential Optical Absorption Spectroscopy (car-MAX-DOAS) measurements and satellite measurements from the Ozone Monitoring Instrument (OMI). On most days, car-MAX-DOAS measurements were carried out along large circles (diameter ~ 35 km) around Paris. The car-MAX-DOAS results are
- compared to coincident data from CHIMERE and OMI. All three data sets have their specific strengths and weaknesses, especially with respect to their spatio-temporal resolution and coverage as well as their uncertainties. Thus we compare them in two different ways: first, we simply consider the original data sets. Second, we compare modified
- ¹⁵ versions making synergistic use of the complementary information from different data sets. For example, profile information from the regional model is used to improve the satellite data, observations of the horizontal trace gas distribution are used to adjust the respective spatial patterns of the model simulations, or the model is used as a transfer tool to bridge the spatial scales between car-MAX-DOAS and satellite observations.
- ²⁰ Using the modified versions of the data sets, the comparison results substantially improve compared to the original versions. In general, good agreement between the data sets is found outside the emission plume, but inside the emission plumes the tropospheric NO₂ VCDs are systematically underestimated by the CHIMERE model and the satellite observations (compared to the car-MAX-DOAS observations). One major
- result from our study is that for satellite validation close to strong emission sources (like power plants or megacities) detailed information about the intra-pixel heterogeneity is essential. Such information may be gained from simultaneous car-MAX-DOAS



measurements using multiple instruments or by combining (car-) MAX-DOAS measurements with results from regional model simulations.

1 Introduction

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Nitrogen oxides (NO_x = NO + NO₂) play an important role in tropospheric chemistry as they impact oxidizing capacity and ozone formation (Atkinson, 2000; Seinfeld and Pandis, 2012). NO_x emissions are dominated by anthropogenic activities, e.g. from traffic and power generation. Emissions from megacities have a strong influence on the regional and global air quality; thus accurate estimates of megacity emissions are highly required. For instance, urban NO₂ concentrations in Paris still represent an important

- ¹⁰ air quality problem (AirParif, 2014), the European annual limit value of $40 \,\mu g m^{-3}$ being exceeded at the urban traffic sites, but also frequently at urban background sites. This calls for further studies including evaluation of urban emissions. One possibility to quantify NO_x emissions from megacities is to use so called "top-down approaches" based on remote sensing observations, e.g. from satellite (Leue et al., 2001; Martin
- et al., 2003; Beirle et al., 2011) or ground based observations (Rivera et al., 2009; Ibrahim et al., 2010; Shaiganfar et al., 2011). Usually top-down emission estimates require inverse modelling or estimates of the atmospheric lifetimes of the considered species. Accordingly, major uncertainties of top-down emission estimates are related to (i) the uncertainties of the remote sensing measurements and (ii) the ability of the models to accurately simulate atmospheric chemistry and physics.

 NO_2 , which typically constitutes the major fraction of NO_x (Seinfeld and Pandis, 2012) can be measured by remote sensing techniques in the visible spectral range (e.g. Brewer et al., 1973; Noxon, 1975; Roscoe et al., 1999). For the estimation of NO_x emissions usually two types of remote sensing measurements: (i) satellite observations (e.g. Leue et al., 2001; Richter and Burrows, 2002; Martin et al., 2002; Beirle et al., 2003; Boersma et al., 2004; Richter et al., 2005) from the Ozone Monitoring Instrument OMI (Levelt et al., 2006), and (ii) so-called Multi-AXis- (MAX-) DOAS obser-



vations (e.g. Hönninger and Platt, 2002; Van Roozendael et al., 2004; Wittrock et al., 2004; Brinksma et al., 2008; Wagner et al., 2011) are used.

In this study we present car-MAX-DOAS observations of tropospheric NO_2 along variable driving routes around Paris during the MEGAOPLI campaign. The work pre-

- sented in this paper investigates the consistency of the car-MAX-DOAS observations with satellite measurements from OMI. In addition to these experimental data sets, also results from a regional chemistry transport model (CTM) CHIMERE (see e.g. Schmidt et al., 2001; Menut et al., 2013) are included in the comparison. In a forthcoming second paper, NO_x emissions from Paris are estimated from the car-MAX-DOAS observations made in circles around Paris, and the resulting emissions are compared to emission inventories (compare e.g. Ibrahim et al., 2010; Wagner et al., 2010; Shaiganfar et
 - al., 2011).

Here it should be noted that since 2005 ground based observations are performed in Paris using a zenith sky instrument (Dieudonné et al., 2013). From these measure-

- ¹⁵ ments important information on the seasonal/diurnal cycle of NO₂ could be derived. In addition, Dieudonné et al. (2013) could show that the NO₂ concentrations systematically decrease with increasing altitude. Modelling with the CHIMERE model of the surface NO_x measurements at three urban and suburban sites during the MEGAPOLI summer campaign (July 2009) showed a reasonable correlation (0.55–0.65), but a sig-
- ²⁰ nificant overestimation between 22 and 95 % (Zhang et al., 2013). Vertically integrated NO₂ column measurements could help to distinguish, if such a bias is due to emissions or two errors in vertical mixing. Deguillaume et al. (2008) used urban NO and O₃ concentrations from the AirParif network to constrain urban and plume ozone concentrations in a Bayesian Monte Carlo framework. The chemical regime over the urban
- ²⁵ area of Paris and within plumes was found clearly VOC sensitive on the average over two summers.

Compared to previous top-down emission inventories based on car-MAX-DOAS measurements (e.g. Rivera et al., 2009; Ibrahim et al., 2010; Shaiganfar et al., 2011), our study is special in many respects:



- (a) Our car-MAX-DOAS measurements cover many days in two seasons (summer 2009 and winter 2009/10). Thus with respect to spatial and temporal coverage our comparison between car-MAX-DOAS and satellite observations goes beyond most existing comparisons (e.g. Brinksma et al., 2008; Chen et al., 2009; Hains et al., 2010; Shaiganfar et al., 2011; Irie et al., 2012; Ma et al., 2013; Lin et al., 2014).
- (b) We systematically compare our measurements with simultaneous satellite and model data sets.
- (c) We make synergistic use by combination of the specific advantages of the differ
 - ent data sets. Thus the specific uncertainties of all used data sets are minimised. The regional model is used as a transfer tool to correct for the differences in spatial resolution.

The paper is organised in the following way: in Sects. 2 and 3 we describe the data sets, their specific advantages and limitations and how to use them in a synergistic way.

¹⁵ In Sects. 4 and 5 CHIMERE model data are compared to car-MAX-DOAS and OMI observations, respectively. Section 6 presents the comparison of coincident observations of all three data sets. A summary and outlook are provided in Sect. 7.

2 Data sets

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The car-MAX-DOAS observations in and around Paris were performed during two extensive measurement campaigns organised in the frame of the MEGAPOLI project (Mahura and Baklanov, 2012; see also http://megapoli.dmi.dk/). In June and July 2009 car-MAX-DOAS measurements were performed on 25 days, and in January and February 2010 on 29 days. For almost all of these days model results from CHIMERE are available. OMI satellite observations are also available for most days, although many of these observations provide only limited information on the tropospheric NO₂ abun-



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dance due to the presence of clouds. The three data sets are discribed in the following sub-sections.

2.1 Car-MAX-DOAS

Car-MAX-DOAS observations were performed by a temperature-stabilised mini-MAX-DOAS instrument which is described in detail in Wagner et al. (2010), Ibrahim et al. (2010) and Shaiganfar et al. (2011). Here a brief overview is given. The MAX-DOAS instrument is mounted on top of a car in backward direction. The telescope (field of view ~ 1.2°) is directed to different elevation angles with integration times of 1 min. The sequence of elevation angles was chosen to: 90°, 5° × 22°, 45°, 5° × 22° (the
messurement sequence is repeated after 12 individual measurements). This choice optimises the number of measurements at low elevation angles, from which we derive the tropospheric VCD. The measurements at elevation angles of 45° and 90° are used for the determination of the NO₂ absorption in the Fraunhofer reference spectrum and are needed at lower frequency (Wagner et al., 2010). For typical driving speeds, this 320–460 nm with a spectral resolution of ~ 0.7 nm (full width at half maximum).

The first step of the data analysis comprises the spectral analysis using the DOAS technique (Platt and Stutz, 2008). From the spectral analysis the integrated NO_2 concentration along the atmospheric light path, the so-called slant column density (SCD) is

- ²⁰ derived. From this NO₂ SCD, the vertically integrated tropospheric NO₂ concentration, the so-called vertical column density (VCD) is derived using the so-called geometric approximation, which assumes direct absorption paths through the tropospheric NO₂ layer (Brinksma et al., 2008; Wagner et al., 2010). The uncertainty of the tropospheric NO₂ VCD derived in this way is typically below 25 % (Shaiganfar et al., 2011). For low
- tropospheric NO₂ VCDs it is dominated by the fit error of the spectral analysis. For high tropospheric NO₂ VCDs it is dominated by the limitations of the geometric approximation (depending on the SZA, the relative azimuth angle, the NO₂ profile and the presence and properties of clouds. Close to strong emission sources, where the



major fraction of NO₂ is located close to the surface, the errors caused by the geometric approximation are small (Shaiganfar et al., 2011). It is also important to note that – depending on the SZA and relative azimuth angle – the application of the geometric approximation can lead to an over- or underestimation of the true tropospheric NO₂

⁵ VCD. Thus, since in this study we analyse a large number of individual car-MAX-DOAS measurements performed during several months in summer 2009 and winter 2009/10, on average the uncertainties caused by the geometric approximation should mostly cancel out.

Different driving routes in and around Paris were used on different days (Fig. 1). On ¹⁰ most days (34 days), measurements around large circles (Fig. 2a) were carried out, usually also including additional measurements closer to the city center (Fig. 2b). On some days also measurements around smaller circles (Fig. 2c) or following different patterns (Fig. 2d) were performed. In the summer campaign, a GPS logger (GPS-Receiver CR4, connected to the Notebook by a USB cable) was used to track the ¹⁵ coordinates of the route along which the measurements were made; during the winter campaign, a mobile GPS (HOLUX m247) was used.

2.2 OMI

OMI was launched in 2004 onboard the Aura satellite (Levelt et al., 2006). It measures spectra of light scattered in the Earth's atmosphere and reflected by the Earth's surface.

²⁰ OMI covers the UV and visible spectral range up to 500 nm, enabling the DOAS retrieval of ozone, NO₂, and other minor trace gases.

Aura is operated on a sun-synchronous orbit, crossing the equator at 1.45 p.m. LT. Spatial resolution is 13 km × 24 km at nadir and decreasing towards the swath edges. Total swath width is 2600 km, resulting in daily global coverage. However, since 2007,

so-called "row anomalies" lead to the dismissing of data for several cross-track positions (Boersma et al., 2011).

In this study, we use operational tropospheric NO_2 VCDs from the DOMINO data product v2.0 (Boersma et al., 2011). Based on the OMI standard NO_2 SCDs (Boersma



et al., 2002), (1) the stratospheric column is removed by assimilation, and (2) tropospheric VCDs are derived based on a-priori vertical profiles, both steps using the TM4 CTM with a longitude–latitude resolution of $3^{\circ} \times 2^{\circ}$.

2.3 CHIMERE

In this paper, simulations are performed with the CHIMERE CTM (Schmidt et al., 2001; Menut et al., 2013) (www.Imd.polytechnique.fr/chimere) developed since 1997 by IPSL (Institute Pierre Simon Laplace) and INERIS (Institut National de l'Environnement Industriel et des Risques). The model is designed to produce daily forecasts of trace gases (e.g. O₃, NO_x) and aerosols (Honoré et al., 2008), as well as long-term (several years) simulations of emission control scenarios using different nesting possibilities (Beekmann and Vautard, 2010).

Simulations are performed with a horizontal resolution of $3 \text{ km} \times 3 \text{ km}$ and a vertical discretization comprising eight vertical layers from ground to about 5 km, with decreasing vertical resolution with altitude.

- Anthropogenic emissions input data are taken from the so-called TNO-MP (MegaPoli) European emission inventory built by the TNO in the framework of the MEGAPOLI project (Valari and Menut, 2008). It is based on the TNO inventory (Kuenen et al., 2014) but incorporates, over four megacities in Europe (Paris, London, Po valley, Rhine-Rhur region), bottom-up emission data compiled by local authorities (e.g.
- ²⁰ Airparif in Paris) (Timmermans et al., 2013). It is characterized by a high spatial resolution, $1/8^{\circ} \times 1/16^{\circ}$ longitude–latitude (roughly 7 km × 7 km). This inventory is described in more details in Kuenen et al. (2014) and Denier van der Gon et al. (2010), and has already been used in several studies (Zhang et al., 2013; Timmermans et al., 2013; Petetin et al., 2014). In addition, Paris NO_x emissions from this inventory have
- ²⁵ been evaluated by Petetin et al. (2014), based on airborne measurements in the Paris plume during the MEGAPOLI summer campaign, showing a probable moderate positive bias (with a best estimation of +29%). Biogenic emissions are computed based



on MEGAN (Model of Emissions of Gases and Aerosols form Nature) emission factors and parametrizations from Guenther et al. (2006).

Meteorological data are produced with the PSU/NCAR Mesoscale Model (MM5; Dudhia et al., 1993). Boundary and initial conditions are taken from the LMDz-INCA2

and LMDz-AERO global models for gaseous and particulate species, respectively (Hauglustaine et al., 2004; Folberth et al., 2006). Landuse data are taken from the 1 km×1 km-resolved GLCF (Global Land Cover Facility) global database (Hansen et al., 2000).

3 Advantages and limitations of the considered data sets

¹⁰ The three data sets differ in many aspects, the most important properties are discussed below.

3.1 Measured quantity

From the satellite and car-MAX-DOAS observations the tropospheric vertical column density (VCD) is derived, which is the vertically integrated NO₂ concentration in the troposphere. No detailed information on the vertical profile can be derived from these observations, because only high elevation angles (angles between the horizontal and the viewing direction) are used. In contrast, the CHIMERE model provides three dimensional NO₂ concentrations fields from which NO₂ vertical columns can be directly calculated. It is worthwhile noting that the model does not extend beyond ~ 5 km above ground level, and thus does not cover the whole troposphere. However, as NO₂ is mostly located in the boundary layer (in particular close to megacities), the potential underestimation of tropospheric column is expected to be small. This is supported by the study of Konovalov et al. (2006) in which the partial tropospheric NO₂ column above

5 km has been estimated as about 0.5×10^{15} mol cm⁻² over the Paris region, thus less than about 10%. Indeed, as NO₂ is mostly located in the boundary layer (in particular



close to megacities), the potential underestimation of tropospheric column is expected to be small. For the comparison with the car-MAX-DOAS measurements the respective underestimation can be fully neglected, because the car-MAX-DOAS observations are only sensitive for atmospheric layers up to about 3 km (Frieß et al., 2006). Instead the NO₂ VCDs extracted from the model slightly overestimate the NO₂ VCDs retrieved from the car-MAX-DOAS measurements.

3.2 Spatial resolution

With typical measurement durations of about 1 min for an individual observation, the spatial resolution of the car-MAX-DOAS derived NO₂ distribution along the driving route is of the order of 1 km. In contrast, the horizontal resolution of the OMI observations is 10 much coarser (at best 13km × 24km, see Sect. 2.2). The horizontal resolution of the CHIMERE simulation is 3 km.

Spatial coverage 3.3

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For most days the measurement strategy was to drive around Paris along large circles (with diameters of about 35 km, see Fig. 3), in order to estimate the total emissions from Paris (Shaiganfar et al., 2011, 2015). Such measurements were carried out once or twice per day. In addition, measurements along smaller circles, and other road seqments were performed on individual days to gain more information on the horizontal NO₂ distribution in the Paris metropolitan area. The satellite provides daily global coverage. However, on many days gaps in the tropospheric NO₂ data are present, due to 20 the presence of clouds or instrumental problems. CHIMERE simulations are performed over an area ranging from 0.35° W to 4.41° E and 47.45 to 50.66° N.

Temporal coverage 3.4

OMI satellite observations over the Paris region are made once per day at around 13:45 local time (LT). Car-MAX-DOAS observations were typically made several times



per day between about 08:00 and 17:00 LT. CHIMERE data are available in hourly time steps.

3.5 Sensitivity and uncertainties

The measurement sensitivity of the car-MAX-DOAS and satellite measurements is systematically different: car-MAX-DOAS observations are most sensitive for layers close to the surface and become increasingly insensitive for altitudes above about 3 km (Frieß et al., 2006). In contrast, the sensitivity of satellite observations decreases towards the surface. This is accounted for in the satellite NO₂ data product used in this study (the "Derivation of OMI tropospheric NO₂ (DOMINO)" product, see Sect. 2.2) based on (relative) a-priori vertical NO₂ profiles from a chemical transport model. However, especially close to strong emission sources, the model profiles can differ strongly from the true NO₂ profiles. Here it is important to note that the uncertainty of the actual NO₂ profile usually constitutes the major uncertainty for satellite observations of the tropospheric NO₂ VCD. The typical uncertainties of the car-MAX-DOAS and satellite measurements are about 25% (Shaiganfar et al., 2011) and 35 to 60%, respectively (Boersma et al., 2004).

The uncertainties of the model data depend on several input parameters, in particular the distribution and strength of the individual emission sources. In addition, also chemical transformations and atmospheric transport play important roles. The orientation and the extent of the simulated emission plume depend critically on wind direction and speed, respectively.

3.6 Effects of clouds

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The sensitivity of satellite observations for tropospheric trace gases is strongly influenced by clouds. In particular if a trace gas is located below a cloud layer, the satellite observations can become almost insensitive. The details of the cloud influence depend on the cloud properties, especially on the cloud fraction (CF) and cloud altitude.



To minimise the cloud influence, often only measurements for small CF are considered. Here only OMI measurements with effective CF below 30% are retained. In contrast to satellite observations, the sensitivity of car-MAX-DOAS measurements is hardly affected by clouds as long as the trace gas is located below the cloud layer (which is a valid assumption close to strong NO_x emission sources).

In summary, the characteristics of the three data sets are quite different; all three data sets have their specific strengths and weaknesses. The main limitations of the satellite observations are their coarse resolution, their large uncertainties, and their strong dependence on cloud cover and the a-priori assumptions on the NO₂ profile. The main limitations of the car-MAX-DOAS observations are their limited spatial and temporal coverage. Also the accuracy of the model data is limited by various uncertainties in emissions, chemistry and transport (e.g. Boynard et al., 2011).

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The main aim of this study is to test the consistency of the three data sets during the two MEGAPOLI measurement campaigns in summer 2009 and winter 2009/10.

- The most direct and usually applied way is the comparison of the original data sets. In addition to these basic comparisons, we also compare modified versions of the three data sets making synergistic use of the strengths and weaknesses of the three different data sets. Here modifications of the model data are of particular importance, because (i) the model results depend critically on the used input data, especially the wind fields
- ²⁰ and the distribution and strength of the emission sources, and (ii) the model data play a crucial role as transfer tool to connect both remote sensing data.

The following corrections to the original data sets are applied in this study:

- (a) The satellite and ground based observations are used to test if the horizontal patterns of the pollution plumes in the CHIMERE simulation are correct. Possible arrors in the direction of the emission plume (due to erroneous wind direction in
- errors in the direction of the emission plume (due to erroneous wind direction in meteorological input data) are corrected by rotating the modelled concentration fields around the center of Paris (see Sects. 4.1 and 5.2).



- (b) The car-MAX-DOAS data are used to test to which detail the model data can resolve the measured horizontal gradients. Different degrees of spatial smoothing are applied to the car-MAX-DOAS data until best match with the model data is achieved (see Sect. 4.2).
- (c) The vertical profiles extracted from the CHIMERE model data are used to improve the satellite retrievals. Compared to the results from the global model used in the original satellite product, the regional CHIMERE model resolves finer spatial gradients (see Sect. 5.1).

Here it should be noted that in cases when rotated CHIMERE data are used (see

point a above), not the original but the rotated CHIMERE profiles are applied to the OMI retrieval. This is an important detail, as the NO_2 profiles vary strongly depending on whether they are inside or outside the emission plume.

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- (d) The car-MAX-DOAS data and model results are used for satellite validation with a specific focus on the effects of clouds on the satellite retrievals (see Sects. 5 and 6).
- (e) The satellite and model data are used to investigate the representativeness of the car-MAX-DOAS data. The model data are used as a transfer tool to bridge the different scales of the MAX-DOAS and satellite observations (see Sect. 6).

Typical examples for the comparison of the three data sets during the Paris campaigns are illustrated in Figs. 3 and 4. Besides the original model data (at 3 km × 3 km resolution), also the re-gridded model data matching the spatial resolution of the satellite observations are shown. Car-MAX-DOAS results are displayed in the plots of the satellite data and separately in a zoomed image (showing also the results of the CHIMERE model). Figure 3 represents a day with almost ideal conditions for the comparison of the different data sets: the satellite covers the whole Paris metropolitan region and only few clouds are present (CF is below 30 % for all satellite pixels). Paris is



pixels is rather small. The car-MAX-DOAS observations cover several OMI ground pixels. Enhanced values of the tropospheric NO₂ VCDs are found at similar locations in all three data sets. However, the pattern of the simulated plume does not exactly match the satellite and car-MAX-DOAS observations: compared to the measurements

- the model plume is slightly rotated clockwise (by about 15°). These discrepancies are likely mostly due to errors in the simulated wind fields, and in particular the wind direction. Figure 4 represents a day with similar conditions, but on that day a field of broken clouds was present over the Paris metropolitan region. While for many of the satellite observations the effective CF is still below 30 %, no enhanced NO₂ VCDs are seen in
- the satellite data (in contrast to the model data and car-MAX-DOAS measurements). This indicates a strong shielding effect of the clouds for the satellite observations of that day. Here it is important to note that usually for low CF the satellite retrievals yield reasonable tropospheric NO₂ VCDs. However, close to strong emission sources, the shielding effect of clouds depends critically on the relative locations of the clouds and the clouds and the strong effect of the satellite is in the satellite observation.
- the areas of enhanced NO₂ concentrations. If e.g. a cloud patch covers an area of high tropospheric NO₂, the satellite data are biased low. If instead the cloud patch covers areas of low tropospheric NO₂, the satellite data are hardly affected by the clouds.

The comparison of the car-MAX-DOAS and model data presented in Fig. 4 again indicates a spatial mismatch between both data sets: the model data would have to be rotated counter-clockwise by about 25° to match the car-MAX-DOAS measurements.

rotated counter-clockwise by about 25° to match the car-MAX-DOAS measurements. In this paper we compare the three data sets in a quantitative way for all days with available car-MAX-DOAS measurements. In addition to the original data sets we compare versions which are modified in different ways as indicated above and described in detail in the respective sections. An overview of the different modifications is presented in Table 1.



4 Comparison between CHIMERE and car-MAX-DOAS

4.1 Spatial patterns and horizontal rotations of the model data

Comparison of the spatial distribution of NO₂ from the CHIMERE model and car-MAX-DOAS measurements generally shows similar spatial patterns, but often reveals
a small "tilt" between both datasets. Here we illustrate this effect and show that correlations between both datasets can be significantly improved if the model data are rotated. Possible reasons for the tilt are discussed below. Fig. 5 shows comparisons between car-MAX-DOAS observations and the CHIMERE results for two selected days (12 February 2010 and 16 July 2009). The identical car-MAX-DOAS data are displayed in all sub-figures, but for CHIMERE, different versions are shown. The top panel presents the horizontal distribution of the simulated tropospheric NO₂ VCDs across the entire area at 13:00 UTC, the approximate median times of the car-MAX-DOAS observations on both days (16 July: 08:25–15:49 UTC; 12 February: 09:57–15:22 UTC). In the middle panel, CHIMERE data are interpolated to the exact times and locations of the individual car-MAX-DOAS observations (coloured squares in the background). On both days different levels of agreement are found: for 12 February 2010 (left) the

spatial patterns of the car-MAX-DOAS measurements and CHIMERE data match quite well, but the absolute values differ. On 16 July 2009 both absolute values and spatial patterns differ.

²⁰ In the lower panel of Fig. 5 the CHIMERE data are rotated around the center of Paris. The rotation angle was determined by optimising the spatial correlation between the car-MAX-DOAS observations and the CHIMERE data (rotation angles are varied in steps of 5° between $\pm 25^{\circ}$). On 12 February 2010 the best agreement was found for a small rotation angle (-5°) whereas on 16 July 2009 the best agreement was found for a larger rotation angle of -15° . After applying the rotations, the agreement of the spatial patterns improved substantially: for 16 July 2009 the correlation coefficient (r^2) increased from 0.66 to 0.81 and the slope increased from 0.48 to 0.58. On 12



February 2009 the influence of the (small) rotation was smaller (r^2 changed from 0.66 to 0.68; the slope changed from 0.29 to 0.30).

We applied rotations to CHIMERE data for all days when car-MAX-DOAS measurements around large circles are available. We chose car-MAX-DOAS measurements

- around large circles, because these observations allow the most accurate determination of the emission plume of Paris. The results of the spatial correlation analyses for the original and rotated CHIMERE data are shown in Fig. 6. The applied rotations cause a substantial improvement of the correlation coefficients. Also the slopes of the regression lines increase while the *y* axis intercepts decrease. However, the slopes are still systematically smaller than unity and the *y* axis intercepts are larger than zero.
- ¹⁰ are still systematically smaller than unity and the *y* axis intercepts are larger than zero indicating an underestimation of the maximum NO₂ VCDs and overestimation of the background NO₂ VCDs by CHIMERE.

In Fig. 7 we show correlation plots between CHIMERE and car-MAX-DOAS data for two selected days: on 16 July 2009 (top) the correlation is largely increased for the rotated CHIMERE data; on 27 July 2009 similar correlation is found for original and rotated CHIMERE data. On both days the slope is close to 0.5 and is hardly affected by the rotation of the CHIMERE data.

The frequency distribution of the optimum rotation angles is presented in Fig. 8. There, in addition to the results of the comparison to the car-MAX-DOAS data, also the

- ²⁰ corresponding results for the comparison to the OMI observations are shown (note that in contrast to Fig. 6 not only measurements around large circles are shown). Somewhat different rotation angles are found for the comparison between car-MAX-DOAS and OMI observations with a correlation coefficient $r^2 = 0.28$ between both sets of the rotation angles. The rather low correlation is probably caused by the fact that the com-
- ²⁵ parisons of the model data with both observational data sets are made for different times and locations. In particular the comparisons vs. OMI observations are performed for a much larger area (see Figs. 3 and 4).

From the comparison of CHIMERE data to both observational data sets counterclockwise rotations are found more frequently than clockwise rotations, with correc-



tions reaching up to 25°. Such differences between simulated and observed surface wind direction of this order are frequently observed for surface winds at the SIRTA site at Ecole Polytechnique, Palaiseau, at 20 km SW from the town center (Zhang et al., 2013). The interesting feature about the present comparison from pollution tracer data is that it harizentally integrates differences over the whole transport distance between

is that it horizontally integrates differences over the whole transport distance between emission sources and the measurement location, and vertically over the effective depth of vertical mixing. An interesting indication from this study is that there could be a bias in this effective transport direction.

4.2 Influence of smoothing to the car-MAX-DOAS data

- In addition to the rotation of the CHIMERE data we also investigated if the resolution of the CHIMERE data matches the spatial gradients observed by car-MAX-DOAS. For that purpose we applied a spatial smoothing (convolution with Gaussian kernels of different widths) to the car-MAX-DOAS results before they are compared to the CHIMERE data. Two of these comparisons are shown in Figs. 9 and 10. Both days were chosen
- ¹⁵ because they represent cases of different improvement after the application of smoothing and rotation. On 21 July 2009 (Fig. 9) best agreement between both data sets is found after the car-MAX-DOAS data are smoothed with a kernel of 4 km (in addition to a rotation of -20°). On 24 January 2010 (Fig. 10) best agreement is found if smoothing kernels between 8 and 12 km are applied (together with a rotation of 10°). But on that
 ²⁰ day even after applying both modifications systematic differences remained.

An overview on the effect of the spatial smoothing for all days is presented in Fig. 11. The results of the correlation analyses (top: correlation coefficients r^2 ; middle: *y* axis intercepts; bottom: slopes) are displayed as a function of the width of the applied smoothing kernel. The thin lines indicate the results for the individual days, and the thick lines

indicate the averages of all days. For both original and rotated CHIMERE data best agreement (highest correlation coefficients and slopes closest to unity) is found after smoothing the car-MAX-DOAS data with kernels of 5 km or larger. As expected, much more consistent results are found for the comparison with the rotated CHIMERE data



(right panel), because without rotation the possible mismatch between both data sets often prevents a meaningful comparison. For the rotated CHIMERE data the optimum smoothing kernels are slightly larger in winter than in summer.

Interestingly, the optimum horizontal smoothing kernels are significantly larger than the spatial resolution of the CHIMERE data (3 km). This result was unexpected, and the potential reasons for the need of an additional smoothing are not completely clear. Probably some atmospheric process(es) relevant for the dispersion of the NO₂ plume are not sufficiently well represented in the model. Such processes might include atmospheric mixing but also the characteristic times of chemical reactions. Alternatively,

- ¹⁰ also the spatial distribution of the emission sources used in the model simulations might be too coarse, or their spatial emission distribution might be imperfect at small scales of some kilometers. In all these cases, smoothing of the spatial scales reduces model errors and improves comparison with observations. A similar results was found by Valari and Menut (2008). They found that smoothing of pollutant emissions to 12 km
- ¹⁵ horizontal resolution gave best results for comparison of CHIMERE simulations over Paris with observed surface ozone (for the case of observed ozone values above the 90 ppb information threshold). This again points to the fact that model processes at smaller scales are probably not well enough represented in the chemistry transport model or its input data.
- Figure 12 presents a comparison of the daily average and maximum values of the tropospheric NO₂ VCDs from car-MAX-DOAS and CHIMERE. The maximum values were determined taking into account data at the locations of the individual car-MAX-DOAS measurements.

The tropospheric NO₂ VCDs show a considerable variation from day to day, which is well represented in both data sets. For the daily averages (Fig. 12a), the smoothing of the car-MAX-DOAS data has almost no effect (as expected). But the daily maxima of the car-MAX-DOAS observations (Fig. 12b) strongly decrease after the smoothing is applied. Furthermore, the agreement between CHIMERE and car-MAX-DOAS results is largely improved after the smoothing. The averaged daily ratios of maximum



and average values are summarised in Table 2. The ratios of the averages for the original and smoothed car-MAX-DOAS data are about 1.01 and 0.87 for summer and winter, respectively, indicating good agreement between both data sets in summer and a systematic underestimation of the car-MAX-DOAS data by CHIMERE in winter. The

- ratios of the daily maxima increase after smoothing from 0.59 to 0.94 in summer and from 0.53 to 0.75 in winter. Despite this considerable improvement, especially in winter, the CHIMERE model systematically underestimates the tropospheric NO₂ VCDs in the Paris plume by about 25%. In Fig. 13 correlation results for the whole summer and winter campaign data sets of individual car-MAX-DOAS measurements vs. the co-
- ¹⁰ incident CHIMERE values are presented for the original and modified data sets. The correlation analyses are performed by an orthogonal linear regression (Cantrell, 2008) because this type of regression analysis, allows considering uncertainties of both compared data sets. The errors of the car-MAX-DOAS measurements are described by a constant (2×10^{15} molec cm⁻²) and a linear term (20%) (see Shaiganfar et al., 2011).
- ¹⁵ Since for the CHIMERE data no error is provided, we simply used the same errors as for the car-MAX-DOAS measurements. The correlation results improve systematically after both modifications, i.e. rotation of CHIMERE data and spatial smoothing of car-MAXDOAS data, with larger improvements in summer. However, still the slopes remain smaller than unity (0.77 in summer and 0.64 in winter) and the *y* axis intercepts larger than zero.

4.3 Quantitative interpretation of the comparison results

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We quantify the agreement of the tropospheric NO₂ background VCDs based on the ratios of the daily average values of CHIMERE vs. car-MAXDOAS (Fig. 12a). For summer, the ratios both for the original and smoothed car-MAX-DOAS data are close to unity (see Table 2) indicating good agreement between both data sets. In contrast, for winter the ratios are lower (0.86 and 0.87 for the original and smoothed car-MAX-DOAS data, respectively) indicating that CHIMERE probably systematically underestimates the car-MAX-DOAS measurements. Here it is, however, interesting to note that



this discrepancy is within the measurement uncertainty of the car-MAX-DOAS observations (see Sect. 2.1).

The agreement of the tropospheric NO₂ VCDs of the emission plume are quantified by the ratios of the daily maxima (Fig. 12b) and the slopes of the regression lines of the individual data pairs (Fig. 13). For the original car-MAX-DOAS data the ratios and slopes are between 0.59 and 0.61 and between 0.52 and 0.53 for summer and winter, respectively. If the smoothed car-MAX-DOAS data are considered, the ratios and slopes are much closer to unity: they are between 0.70 and 0.94 and 0.64 and 0.75 in summer and winter, respectively. But they still indicate a strong and systematic underestimation by CHIMERE.

Here it should be noted that similar results are found if in addition to the measurements along the large circles also the measurements in the city center on the same days are considered (Fig. S1a in Supplement). Also for all coincident measurements similar results are obtained (Fig. S2 in Supplement), but the correlations become ¹⁵ worse, because in many cases the rotation angle of the CHIMERE data is less well constrained than for the large circles. Note that for larger smoothing lengths (higher sigma), slopes close to 1 and intercepts close to 0 can be reached (Fig. 11), while correlation coefficients again decrease. However, for lengths above 10 km, the Paris emission plume becomes less and less resolved.

5 Comparison between CHIMERE and OMI

5.1 Influence of the selected NO₂ profiles on the satellite data

The tropospheric NO₂ VCD retrieved from OMI depends systematically on the (relative) NO₂ profile used in the inversion process (Boersma et al., 2011). For the OMI version used in this paper (DOMINO v2.0) the NO₂ profiles are taken from the TM4-model (Boorsma et al., 2007, 2011), which has a spatial resolution of 2° in latitudinal and 3° in

²⁵ (Boersma et al., 2007, 2011), which has a spatial resolution of 2° in latitudinal and 3° in longitudinal direction. It has 34 vertical layers below 0.38 hPa with the vertical resolution



of the lowest layer of about 25 m. Due to the rather coarse horizontal resolution, the model is probably not capable to resolve spatial gradients close to strong emission sources. In particular, in such cases the simulated NO₂ profiles probably underestimate the enhanced concentrations close to the ground. To investigate the influence of the

- ⁵ NO₂ profile on the OMI results in more detail we compared the NO₂ profiles from the TM-4 model over Paris with the corresponding profiles from the CHIMERE model (with a much higher spatial resolution of 3 km × 3 km) for selected OMI observations. In Fig. 14 NO₂ profiles in the Paris plume and for "background" levels are shown for 4 July 2009. For the OMI pixel in the plume the CHIMERE profile shows much higher NO₂
- concentrations for altitudes < 1 km than the TM-4 model. Replacing the TM-4 profiles by the CHIMERE profiles in the satellite data retrieval leads to smaller air mass factors and thus to higher tropospheric NO₂ VCDs: for the measurements of the emission plume shown in Fig. 14 the tropospheric NO₂ VCD increases by about a factor of two. In contrast, for measurements outside the emission plumes the values hardly change.
 Similar results are found for the other measurement days.

Thus in all further comparisons of this study, in addition to the original DOMINO v2.0 product, we also consider the OMI results retrieved using the CHIMERE profiles (this version is referred to as modified OMI data).

Here it is important to note that, although the modified OMI data are partly dependent on the CHIMERE profiles, it still makes sense to compare the modified OMI data to the tropospheric NO₂ VCDs extracted from the CHIMERE data, because the modified OMI data only depend on the relative shape of the simulated NO₂ profile, but not on the absolute value of the tropospheric NO₂ VCD.

5.2 Influence of horizontal rotations of the model data on the comparison with OMI

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As for the car-MAX-DOAS data, we investigated the effects of rotations of the CHIMERE results around the center of Paris on the comparison with the OMI data. Two examples are shown in Figs. 15 and 16. On 28 July 2009 (Fig. 15) the emission



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plume extended in north-east direction. Good spatial agreement between the model simulations (re-sampled to OMI ground pixel extent) and satellite observations is found after the model data is rotated by -20° . On that day the simulated tropospheric NO₂ VCDs are systematically underestimated compared to OMI data, especially far away

- from the city center (of course, in principle, also the OMI data might have a systematic offset). The differences between model simulations and satellite observations become even larger for the modified OMI product because for observations of the most polluted areas the replacement of the TM-4 profile by the CHIMERE profile has the strongest effect.
- ¹⁰ In Fig. 16 results for 8 February 2010 are shown. Although the CF is > 30 % for all OMI measurements on that day, we chose this example to illustrate that even under such unfavourable conditions the satellite observations can yield useful information on the location of the emission plume. Like for the previous example, good agreement between both data sets is found after the CHIMERE data is rotated by -25° . And also
- the model data are again systematically smaller than the satellite observations. In spite of the strong influence of clouds on the satellite observation on 8 February 2010, it is interesting to note that the OMI data show enhanced tropospheric NO₂ VCDs at similar locations as the model.

Note that similar comparisons between the three data sets for all days of both car-²⁰ MAX-DOAS campaigns are presented in the Supplement (Fig. S4). Here it should again be noted that for the modified OMI data (see Sect. 5.1) not the original but the rotated CHIMERE profiles were applied to the OMI retrieval. This is an important detail, as the NO₂ profiles vary strongly depending on whether they are inside or outside the emission plume.

²⁵ In Fig. 17 the results of spatial correlation analyses between CHIMERE and OMI for all days with coincident measurements are shown. Like for the comparison with the car-MAX-DOAS measurements, for most days the rotation of the CHIMERE data leads to an improvement of the correlation coefficients. However, for the slopes and *y* axis intercepts only small changes are found.



Figure 18 presents the daily averages and maxima for both data sets for effective CF < 30 %. Like for the comparison between car-MAX-DOAS and CHIMERE, the day to day variability is well represented in both data sets. The average ratios of daily maximum and average values are summarised in Table 3. For the ratios of the averages the

- ⁵ modification of the OMI data using the CHIMERE profiles has a small effect. The ratio between CHIMERE and OMI data is about 0.76 in summer and 1.00 in winter. Concerning the maxima, the effect of the modification of the OMI data using the CHIMERE profiles is stronger: the ratios between CHIMERE and OMI data decrease from 0.83 to 0.68 in summer and from 0.85 to 0.80 in winter.
- Figure 19 presents the correlation results between CHIMERE and OMI for all individual data pairs. In addition to the original OMI (v2.0) and CHIMERE data also results for the rotated CHIMERE data and the modified OMI data are shown. Again an orthogonal linear regression is performed, where the uncertainties of the CHIMERE data are described by a constant $(2 \times 10^{15} \text{ molec cm}^{-2})$ and a linear term (20%). For OMI the individual errors are taken from the DOMINO data product (Boersma et al., 2011).
- After each modification step the correlations between both data sets improve (r^2 increases from 0.31 to 0.71 in summer and from 0.24 to 0.50 in winter). In contrast, the slopes of the regression lines hardly changes (in winter they even decrease). For the comparison between the rotated CHIMERE and the modified OMI data, the slopes are 0.52 and 0.06 respectively (but for winter the slopes has to interpreted with ears
- ²⁰ are 0.52 and 0.96, respectively (but for winter the slope has to interpreted with care, because of the rather poor correlation).

5.3 Quantitative interpretation of the comparison results

We quantify the agreement of the tropospheric NO₂ background VCDs based on the ratios of the daily average values (Fig. 18a). For winter, the ratios both for the original and the modified OMI data are close to unity (see Table 3) indicating good agreement between both data sets. In contrast, for summer the ratios are much lower (0.74 and 0.76 for the original and modified OMI data, respectively) indicating that CHIMERE systematically underestimates the OMI measurements.



The agreement of the tropospheric NO_2 VCDs in the Paris plume is quantified by the ratios of the daily maxima (Fig. 18b) and slopes of the regression lines of the individual data pairs (Fig. 19). For the original OMI data, the ratios and slopes are between 0.52 and 0.83 and between 0.85 and 1.16 for summer and winter, respectively. Overall, these results indicate a systematic underestimation of the OMI data by CHIMERE (the slope of 1.16 is probably not very meaningful because of the rather low correlation coefficient).

If the modified OMI data are considered, the ratios and slopes become even smaller: they are between 0.52 and 0.68 and 0.80 and 0.90 in summer and winter, respectively.

¹⁰ This finding reflects the fact that the use of the CHIMERE profiles causes an increase of the OMI results. However, the use of the CHIMERE profiles (instead of the original TM-4 profiles) is justified by the substantial improvement of the correlation coefficient.

6 Comparison between OMI and car-MAX-DOAS

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In this section we first directly compare car-MAX-DOAS to OMI observations. Then we use the CHIMERE model as a transfer tool to correct for the differences in the spatial coverage.

For the comparison between car-MAX-DOAS and OMI data we averaged all MAX-DOAS measurements within each OMI ground pixel with effective CF below 0.3, for days where large circles around Paris are sampled. Like for the comparison between

- ²⁰ CHIMERE and car-MAX-DOAS data (Sect. 4), the choice for large circles was made because for these observations the rotation of the CHIMERE data can be more accurately determined. The rotation angle was determined from the comparison to the car-MAX-DOAS data (see Sect. 4). The (rotated) CHIMERE profiles were used for the modification of the OMI data.
- In Fig. 20 the averages of the daily maximum and average values of the different data sets are compared. Overall, the day to day variability of the tropospheric NO₂ VCDs is well captured by the three data sets. Here it should be noted that in Fig. 20



two versions of the CHIMERE data are used: CHIMERE (OMI) indicates CHIMERE results averaged over the entire OMI ground pixels, whereas CHIMERE (DOAS) indicates CHIMERE results averaged for the locations of the coincident car-MAX-DOAS observations. Especially for the maximum values, the specific sampling of the model
 data has a substantial effect: CHIMERE data sampled at the locations of the car-MAX-DOAS observations are systematically larger than the CHIMERE data sampled over the entire OMI ground pixels indicating the effect of spatial gradients within the satellite ground pixels.

In Table 4 the average ratios of the daily maximum and average values are shown. In summer, similar ratios for the averages and maxima (about 0.90) are derived for the original and smoothed car-MAX-DOAS data. If, however, the car-MAX-DOAS data are scaled to full OMI pixels, the ratios between OMI and car-MAX-DOAS data becomes close to unity. The correction for the effect of spatial gradients is performed by multiplying the car-MAX-DOAS data by the average ratio CHIMERE (OMI)/CHIMERE (DOAS), which is ~ 0.90).

For winter, again similar ratios for the averages and maxima are found for the original and smoothed car-MAX-DOAS data, but now they are much lower (around 0.60). After correction for the effect of spatial gradients within the satellite ground pixels, the ratios increase from 0.72 to 0.82, but still are systematically below unity indicating that the OMI results underestimate the car-MAX-DOAS data.

The results of the correlation analyses for individual measurements are shown in Fig. 21. Again an orthogonal linear regression is performed, where the uncertainties of the car-MAX-DOAS data are described by the SD of the individual observations divided by the number of observations inside the OMI pixels. For OMI the individual errors are taken from the DOMINO data product (Boersma et al., 2011).

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The different sub-plots show results for different versions of the car-MAX-DOAS data: original car-MAX-DOAS data (Fig. 21a), smoothed car-MAX-DOAS data (Fig. 21b) and scaled car-MAX-DOAS (Fig. 21c). Here the car-MAX-DOAS data are again scaled to the full OMI pixels, but now the correction is applied for individual car-MAX-DOAS



measurements using the respective ratios CHIMERE (OMI)/CHIMERE (DOAS). The correction of the car-MAX-DOAS data leads to a much better agreement between both data sets: the correlation coefficients *r*² increase from 0.29 to 0.49 in summer, and from 0.64 to 0.73 in winter. The slopes increase from 0.49 to 0.85 in summer, and from 0.56 to 0.77 in winter. It should, however, be noted that the slopes of the regression lines are still smaller than unity indicating that OMI underestimates the tropospheric NO₂ VCD in the emission plume of Paris.

6.1 Quantitative interpretation of the comparison results

We quantify the agreement of the tropospheric NO₂ background VCDs based on the ratios of the daily average values (Fig. 20). For summer, the ratios are 0.90 and 0.97 for the original and scaled car-MAX-DOAS data, respectively, indicating a slight underestimation of the car-MAX-DOAS data by OMI. For winter, the ratios are much smaller: they are 0.56 and 0.72 for the original and scaled car-MAX-DOAS data, respectively, indicating a strong underestimation of the car-MAX-DOAS data by OMI.

- ¹⁵ The agreement of the tropospheric NO₂ VCDs of the emission plume is quantified by the ratios of the daily maxima (Fig. 20) and slopes of the regression lines of the individual data pairs (Fig. 21). For the original car-MAX-DOAS data, the ratios and slopes are between 0.48 and 0.91 and between 0.56 and 0.58 for summer and winter, respectively, indicating a substantial underestimation of the car-MAX-DOAS data by
- OMI. If the scaled car-MAX-DOAS data are considered, the ratios and slopes increase: they are between 0.85 and 1.00 and between 0.77 and 0.82 in summer and winter, respectively, indicating a weaker, but still systematic underestimation of the car-MAX-DOAS data by OMI.

We also compared the original OMI data (v2.0) to the car-MAX-DOAS observations (see Fig. S3 in the Supplement). Like for the modified OMI data better agreement is found after applying the correction for the spatial gradients inside the OMI ground pixels to the car-MAX-DOAS data. However, the correlation coefficients and slopes are much smaller than for the comparison with the modified OMI data indicating the importance





to use appropriate NO_2 profiles for the processing of the satellite data close to strong emission sources.

6.2 Comparison with the results of Sects. 4 and 5

The data selection in this section is quite different compared to the selections for the bilateral comparisons presented in Sects. 4 and 5. Especially for the comparison between OMI and CHIMERE much larger areas are covered in Sect. 5. Thus it is interesting to see how the different data selections affect the comparison results. In Table 5 the respective ratios of daily averages and maxima as well as the results of the regression analyses are compared for the different data selections.

- ¹⁰ For the comparison between CHIMERE and car-MAX-DOAS slightly higher ratios are found if only coincident CHIMERE and car-MAX-DOAS data are compared (the additional constraint of coincident OMI observations mainly excludes cloudy situations from the comparison, because only OMI observations with effective CF below 0.3 are considered). This finding probably indicates that car-MAX-DOAS observations under
- ¹⁵ mostly overcast conditions slightly underestimate the true tropospheric NO₂ VCD, because a small fraction of the tropospheric NO₂ VCDs might be inside the cloud layer.

For the comparison between CHIMERE and OMI similar ratios are found for winter, but in summer CHIMERE underestimates the OMI observations more than for the comparison presented in Sect. 5. This discrepancy is probably related to the fact that

- the observations selected in Sect. 5 cover a much larger area around Paris and indicates that the underestimation of the OMI data by CHIMERE increases with increasing distance from the emission source. One possible explanation for this finding is that the underestimation of the NO_x lifetime in the CHIMERE model (potentially due to too high OH levels). Another possibility could be that the NO₂ profiles used in the OMI analysis might be more appropriate close to the emission sources.
- ²⁵ might be more appropriate close to the emission sources.

7 Summary and outlook

In this study we compared extensive data sets of tropospheric NO₂ VCDs obtained from car-MAX-DOAS observations in the Paris metropolitan area with coincident satellite measurements from OMI and results from the regional model CHIMERE. The car-

- MAX-DOAS measurements were carried out on 25 days in summer 2009 and 29 days in winter 2010 within the European research project Megapoli (Mahura and Baklanov, 2011). On most of these days car-MAX-DOAS measurements were made along large circles (diameter ~ 35 km) around Paris. The duration of individual car-MAX-DOAS measurements was about one minute corresponding to about 1 km. The car-MAX-DOAS measurements were primarily made to determine the entire NO_x emissions from Paris (see e.g. Shaiganfar et al., 2011). The derived NO_x emissions will be published
- in a separate paper (Shaiganfar et al., 2015). In this study we focus on the direct comparison of the car-MAX-DOAS results with the two other data sets.

All three data sets all have their specific strengths and weaknesses, especially with respect to their spatio-temporal resolution and coverage as well as their uncertainties. Car-MAX-DOAS have rather small uncertainties and high spatial resolution, but provide only small spatio-temporal coverage. Satellite observations cover the area of interest on a daily basis, but with a rather coarse spatial resolution and relatively large uncertainties. The influence of clouds on the satellite results is strong, and usually only measurements with low effective CF provide meaningful information on the tropospheric

surements with low effective CF provide meaningful information on the tropospheri NO_2 VCD (here we use measurements with effective CF below 30 %).

First we directly compare the original versions of the three data sets. Here, rather large systematic differences and low correlations are found. In particular the enhanced NO₂ VCDs inside the emission plume from Paris measured by car-MAX-DOAS are

²⁵ largely underestimated by the satellite observations and model results. In a second attempt, we compare the three data sets after they were modified by making synergistic use of the specific advantages of the different data sets:



 CHIMERE model results were rotated around the center of Paris until best spatial agreement with car-MAX-DOAS or satellite measurements was obtained. The observation of a "tilt" between the spatial patterns of CHIMERE and MAX-DOAS are probably related to errors in wind speed in the MM5 meteorological model.

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- Car-MAX-DOAS measurements were spatially smoothed until best match with the model data was achieved. The resulting smoothing Kernels of about 6–8 km suggest an effective resolution of CHIMERE of this order.
- OMI data were corrected by using the vertical NO₂ concentration profiles from the regional CHIMERE model.
- The effect of spatial gradients within the satellite ground pixels on the comparison between car-MAX-DOAS and OMI observations was accounted for and partially corrected using the CHIMERE model data.

The last two points underline the need for a regional model in order to compare MAX-DOAS with satellite measurements in a meaningful way.

Using these modified data sets, the correlation of individual data pairs largely improved. Also, much better quantitative agreement between the data sets was found. However, still the satellite observations and the CHIMERE model results systematically underestimate the car-MAX-DOAS observations inside the emission plume from

Paris, although the underestimation is much less compared to the original data sets. For the tropospheric NO₂ VCDs outside the emission plume, a much better agreement is found.

From these results we conclude that close to strong emission sources, the applied improvements of the observational and simulation data sets are essential for a mean-

²⁵ ingful quantitative comparison of the tropospheric NO₂ VCDs: for example in the measurements in the Paris metropolitan area, about 10 to 40 % of the observed differences can be attributed to effects of spatial gradients (see also Chen et al., 2009; Ma et al.,



2013; Lin et al., 2014). By not properly considering these effects, wrong conclusions on the accuracy of the considered data sets of the same order may be drawn. Information on the spatial gradients within the satellite ground pixels may be obtained e.g. by simultaneously using multiple car-MAX-DOAS measurements, or by combining (car-) MAX-DOAS measurements with results from a regional model. Similar changes of the

absolute values may occur if inappropriate vertical profiles are used in the satellite data analysis.

One additional interesting finding of our study is that in summer the underestimation of the OMI observations by the CHIMERE model increases with increasing distance from the emission source. This finding could indicate a too low atmospheric NO_x life-

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time in the model simulations. We suggest that future studies should use more sophisticated methods for the extraction of the tropospheric NO₂ VCD from car-MAX-DOAS measurements than the

geometric approximation. In particular radiative transfer simulations should be applied taking into account the dependence from SZA and relative azimuth angle. Improved car MAX-DOAS results will especially be important for the validation of new satellite measurements with largely improved spatial resolution (like the future satellite missions Sentinel-5 precursor, Sentinel 4 and 5, see Ingmann et al., 2012; Veefkind et al., 2012).

²⁰ The Supplement related to this article is available online at doi:10.5194/amtd-8-2437-2015-supplement.

Acknowledgements. The research leading to these results has received funding from the European Union's Seventh Framework Programme FP/2007–2011 within the project "MEGAPOLI", grant agreement n° 212520. We acknowledge the free use of tropospheric NO₂

²⁵ column data from the OMI sensor from www.temis.nl. We are very thankful to several drivers, who supported the car-MAX-DOAS measurements: Thierry Marbach, Tobias Tröndle, Steffen Dörner, Christoph Hörmann, Bastian Jäcker, Sven Krautwurst.



The article processing charges for this open-access publication have been covered by the Max Planck Society.

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Table 1. Overview on the different qiantities used in this study.

Quantity	Description
Original car-MAX-DOAS data	Tropospheric NO ₂ VCDs for a given off-zenith eleva- tion angle, determined using the geometric approxi- mation.
Smoothed car-MAX-DOAS data	Horizontally smoothed tropospheric NO_2 VCDs using Gaussian functions with sigma values of 6 and 8 km for summer and winter, respectively.
Scaled car-MAX-DOAS data	Average of smoothed car-MAX-DOAS data over an OMI pixel divided by the ratio of CHIMERE(DOAS)/CHIMERE(OMI).
Original CHIMERE data	Vertically integrated NO_2 concentrations (tropo- spheric NO_2 VCD) for a 3km × 3km CHIMERE grid.
Rotated CHIMERE data	CHIMERE data rotated around the center of Paris to match the car-MAX-DOAS or OMI data.
CHIMERE(DOAS)	(rotated) CHIMERE data averaged for the locations of all car-MAX-DOAS inside an OMI pixel.
CHIMERE(OMI)	(rotated) CHIMERE data averaged over the whole OMI pixel.
Original OMI data	Tropospheric NO ₂ VCD derived from OMI observa- tions (DOMINO product, v2.0).
Modified OMI data	Tropospheric NO_2 VCD derived from OMI observa- tions using the NO_2 profile from rotated CHIMERE instead of the TM-4 model.



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Table 2. Ratios of daily average and maximum values (CHIMERE/car-MAX-DOAS) as well as slopes and correlation coefficients of the regression analyses for measurements at large circles.

Quantity	Ratio CHIMERE/original car-MAX-DOAS		Ratio CHIMERE/smoothed car-MAX-DOAS		
	Summer	Winter	Summer	Winter	
Ratio of averages	1.01	0.86	1.01	0.87	
Ratio of maxima Slope (r^2)	0.59 0.61 (<i>r</i> ² = 0.63)	0.53 0.52 ($r^2 = 0.47$)	0.94 0.70 ($r^2 = 0.77$)	0.75 0.64 $(r^2 = 0.54)$	

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Table 3. Ratios of daily average and maximum values (CHIMERE/OMI) as well as slopes and correlation coefficients of the regression analyses for OMI observations with effective CF below 0.3.

Quantity	Ratio CHIMEI Summer	RE/OMI (v2.0) Winter	Ratio CHIMERE/modified OMI	
Ratio of averages	0.74	0.99	0.78	1.00
Ratio of maxima Slope (r^2)	0.83 0.52 ($r^2 = 0.46$)	0.85 1.16 (<i>r</i> ² = 0.35)	0.68 0.52 ($r^2 = 0.71$)	0.80 0.90 $(r^2 = 0.50)$

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Table 4. Ratios of daily average and maximum values (modified OMI/car-MAX-DOAS) as well as slopes and correlation coefficients of the regression analyses for measurements at large circles and OMI effective CF below 0.3. For the correction of the car-MAX-DOAS observations see text.

Quantity	Modified OMI/original car-MAX-DOAS		Modified OMI/scaled car-MAX-DOAS		
	Summer	winter	Summer	Winter	
Ratio of averages	0.90	0.56	0.97	0.72	
Ratio of maxima Slope (r^2)	0.91 0.48 (<i>r</i> ² = 0.29)	0.58 0.56 ($r^2 = 0.64$)	1.00 0.85 (<i>r</i> ² = 0.49)	0.82 0.77 (<i>r</i> ² = 0.73)	

Table 5. Summary of the quantitative comparisons between the three data sets for different data selections. The background results are derived from the ratios of the daily averages. The results for the emission plumes are derived from the ratios of the daily maximum values and the correlation analyses of the individual observations. Note that for both data selections the results for the comparison between OMI and car-MAX-DOAS are the same, because CHIMERE data are available for all days.

(a) Coincidences of all three data sets

Case	CHIMERE ^a /DOAS ^b		OMI ^c /DOAS ^b		CHIMERE ^a /OMI ^c	
	Summer	Winter	Summer	Winter	Summer	Winter
Background	1.01	0.87	0.97	0.72	0.78	1.00
Emission plume	0.70–0.94	0.64–0.75	0.73–0.82	0.85–1.00	0.52–0.68	0.80-0.90
(b) Coincidences of two data sets						
Case	CHIMERE ^a /DOAS ^b		OMI ^c /DOAS ^b		CHIMERE ^a /OMI ^c	
	Summer	Winter	Summer	Winter	Summer	Winter
Background	0.93	0.69	0.97	0.72	0.98	0.92
Emission plume	0.78–0.96	0.45–0.68	0.73–0.82	0.85–1.00	0.97–1.04	0.81–0.93

^a Rotated CHIMERE.

^b Scaled car-MAX-DOAS.

^c Modified OMI.





Figure 1. Typical driving routes around Paris with different radii. The numbers indicate: 1: small circle (Périphérique), 2: intermediate circle, 3: large circle, 4: Eiffel tower, 5: Airport, 6: Stade de France, 7: Creteil, 8: Palace of Versailles.







Figure 2. Typical car-MAX-DOAS results. (a) Measurements around large circles; (b) measurements around large circles and in the city center; (c) measurements around small circles; (d) measurements at other road segments.



Figure 3. Comparison of the tropospheric NO2 VCDs accross the Paris metropolitan area derived from model simulations, satellite observations and car-MAX-DOAS observations on 16 July 2009. (a) CHIMERE model results at the time of the OMI overpass (12:54) at original resolution; (b) CHIMERE results averaged for the individual OMI ground pixels; (c) MODIS RGB image; (d) OMI v2.0 data together with car-MAX-DOAS results; (e) same as (d) but for cloud fraction below 30 %; (f) car-MAX-DOAS results (small circles) together with CHIMERE model results extracted for the same time and location of the car-MAX-DOAS data (large squares). The car-MAX-DOAS measurements were performed between 08:25 and 15:49 UTC; the measurements around the large circle were performed between 10:07 and 14:05 UTC.







Figure 4. Same as Fig. 3 for the 25 July 2009. OMI overpass was on 12:47 UTC; the car-MAX-DOAS measurements were performed between 8:26 and 14:53 UTC; the measurements around the large circle were performed between 11:37 and 14:07 UTC.



Figure 5. Comparison of car-MAX-DOAS observations with model results for 12 February 2010 (left) and 16 July 2009 (right). Top: CHIMERE data at the center time of the car-MAX-DOAS observations (13:00 UTC); Middle: CHIMERE data interpolated in space and time to match the individual car-MAX-DOAS observations; Bottom: rotated CHIMERE data interpolated to the car-MAX-DOAS observations.











Figure 7. Correlation analyses of original (left) and rotated (right) CHIMERE data vs. coincident car-MAX-DOAS observations for two selected days. On 16 July 2009 (top) the rotation substantially improves the correlation. On 27 January 2010 the rotation only leads to a slightly improved correlation.





Figure 8. Frequency distribution of the optimum rotation angles for the comparison of the CHIMERE data with car-MAX-DOAS observations (blue) and satellite observations (green). Here not only results for large circles (like in Fig. 6), but for all measurements are shown.











Figure 10. Same as Fig. 9, but for 24 January 2010.





Figure 11. Results of the spatial correlation analyses between CHIMERE and car-MAX-DOAS data for individual days (thin lines) as function of the smoothing kernel (measurements along large circles). The thick lines indicate the averages of the individual days. Left: original CHIMERE data; right: rotated CHIMERE data. The vertical lines indicate the smoothing kernels, for which the highest correlation coefficients are found.





Figure 12. Comparison of the daily average (a) and maximum (b) tropospheric NO_2 VCDs for original and smoothed car-MAX-DOAS observations (all data) and coincident CHIMERE data.





Figure 13. Correlation analyses between CHIMERE and car-MAX-DOAS observations (along large circles) for **(a)** the original data sets, **(b)**, rotated CHIMERE data, and **(c)** rotated CHIMERE data and smoothed car-MAX-DOAS data.



Discussion Paper





Figure 14. (a) Comparison of the vertical NO₂ profiles from TM-4 and CHIMERE for locations inside or outside the emission plume on 4 July 2009; **(b)** near-surface (0–44 m) NO₂ concentrations from CHIMERE and locations of the selected profiles; **(c)** OMI results from the operational product (v2.0); modified OMI results using the NO₂ profiles from the regional CHIMERE model.



Figure 15. Comparison of different versions of OMI and CHIMERE data for 28 July 2009. Also shown are a MODIS RGB image and the car-MAX-DOAS results of that day.



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Figure 16. Comparison of different versions of OMI and CHIMERE data for 8 February 2010. Also shown are a MODIS RGB image and the car-MAX-DOAS results of that day.



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Figure 17. Results of the spatial correlation analyses between CHIMERE and OMI (v2.0 for CF < 30 %) for individual days (dots: results for original CHIMERE data; stars: results for rotated CHIMERE data). (a): correlation coefficients; (b) slopes of the regression lines; (c) y axis intercepts; (d) optimum rotation angles.





Figure 18. Comparison of the daily average (a) and maximum (b) tropospheric NO_2 VCDs for original and modified OMI observations (CF below 30%) and coincident CHIMERE data.





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Figure 19. Correlation analyses between CHIMERE and OMI observations (for CF < 30 %) for (a) the original data sets, (b), rotated CHIMERE data, and (c) rotated CHIMERE data and modified OMI data.



Figure 20. Comparison of the daily average **(a)** and maximum **(b)** tropospheric NO₂ VCDs for coincident data of all three data sets (car-MAX-DOAS measurements along large circles and OMI observations for CF < 30%; rotated CHIMERE data).





Figure 21. Correlation analyses between OMI observations (modified version for CF < 30%) and different versions of car-MAX-DOAS observations (along large circles). **(a)** original car-MAX-DOAS; **(b)** smoothed car-MAX-DOAS; **(c)** car-MAX-DOAS corrected for spatial gradients within the satellite ground pixels (see text).



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