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Comparison and evaluation of modelled and GOME measurement derived tropospheric NO_2 columns over Western and Eastern Europe

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Abstract

We present the results of a first comparison of the tropospheric NO_2 column amounts derived from the measurements of the Global Ozone Monitoring Experiment (GOME) with the simulated data from a European scale chemistry transport model (CTM) which is distinctive from existing global scale CTMs in higher horizontal resolution and more detailed description of the boundary layer processes and emissions. We employ, on the one hand, the newly developed extended version of the CHIMERE CTM, which covers both Western and Eastern Europe, and, on the other hand, the most recent version (Version 2) of GOME measurement based data-products, developed at the University of Bremen. We evaluate our model with the data of ground based monitoring of ozone and verify that it has a sufficiently high level of performance, which is expected for a state-of-the-art continental scale CTM. The major focus of the study is on a systematic statistical analysis and a comparison of spatial variability of the tropospheric NO_2 columns simulated with CHIMERE and derived from GOME measurements. The analysis is performed separately for Western and Eastern Europe using the data for summer months of 1997 and 2001. In this way, we evaluate the upper limits to uncertainties of spatial distributions of the considered data. Specifically, for Western Europe, it is found that the mean relative (multiplicative) random errors of the GOME measurement derived and simulated data averaged over the summer seasons considered do not exceed 25% and 35%, respectively, and the mean absolute (additive) errors are less than $3{\cdot}10^{14}$mol/cm^2. The upper limits for the multiplicative errors for Eastern Europe are shown to be smaller than those for Western Europe and do not exceed 15% and 24% for NO_2 columns from GOME and CHIMERE, respectively. The relative contribution of the additive errors is found to be much larger for Eastern Europe, but their mean absolute values are less than $2{\cdot}10^{14}$mol/cm^2.

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1. Introduction

It is well known that in many instances air pollution by photo-oxidants has a non-local origin and that polluted air may be transported within the atmosphere over hundreds and even thousand of kilometres. The recognition of such a fact has fostered development of chemistry transport models (CTM) of the continental scale with the horizontal resolution of several tenths of kilometres, such as EMEP (see, e.g., Simpson et al., 2003), DEM (Zlatev et al., 1992), LOTOS (Builtjes, 1992), EURAD (Hass et al., 1995), CHIMERE (Schmidt et al., 2001), and others (see, e.g., Byun and Ching, 1999 for more references). Most of the existing European continental scale CTMs are focused on Western Europe, although some of them (e.g., EMEP and LOTOS) take into account also a part of Eastern Europe. It is obvious that a model with a larger domain, but nevertheless a good horizontal resolution, may not only be used to study transport processes on a larger scale but, besides, it may enable a broader insight into regularities and climatological features of atmospheric processes in different environments. Moreover, taking into account that continental scale CTMs are designed to simulate the fate of air pollution within the boundary layer more accurately than the global models, the development of continental scale models for major populated regions contributes eventually to validation of available emission data and, consequently, to better understanding of the chemical balance of the troposphere and the atmosphere in general. However, the extension of European CTMs beyond the Western Europe presents rather serious difficulties, because the amount of available observational data needed to specify model parameters, and, especially, to validate model results outside Western Europe is rather limited. For example, only two stations out from more than 100 ones in the EMEP ground based ozone monitoring network are operating in Russia, and some other former USSR countries, e.g., Ukrainia and Byelorussia have no ozone measuring EMEP stations at all. The situation with measurements of ozone precursors in the mentioned countries is even worse. Therefore, as soon as modelling photo-oxidant air pollution over Eastern Europe is concerned, the traditional way of validation of conti-

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nental scale CTMs via comparison of simulations with ground based observations of the key species (see, e.g., Fagerli et al., 2003) turns out to be of very limited utility.

Meanwhile, a significant source of global observational information concerning the atmospheric pollution, namely, satellite measurements of trace gases in the troposphere, has become available in recent years. It has been shown, in particular, that measurements performed by the satellite borne instrument of Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999) can be used to retrieve the tropospheric column amounts of nitrogen dioxide and several other trace gases (see, e.g., Velders et al., 2001; Richter and Burrows, 2002; Martin et al., 2002). More recently, the data retrieved from the measurements of the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) featuring higher spatial resolution than GOME instrument have also become available (e.g., Buchwitz et al., 2004), but these data still have a preliminary and fragmentary character.

Although it is obvious, that comparison with NO_2 columns cannot provide enough information about the overall model performance (concerning, e.g., predictions of ozone concentrations), it may shed some light on a degree of uncertainty of input NO_x emission data and of the quality of representation of major oxidation and transport processes which take an important part in variability of other important photo-oxidants and their precursors. Besides, modelling of nitrogen dioxide is important by itself, taking into account that NO_2 plays an important part in the photochemistry of both the boundary layer and free troposphere (see, e.g., Kley et al., 1999; Bradshaw et al., 2000) and contributes to radiative forcing of the climate (Solomon et al., 1999; Velders et al., 2001). Finally, comparison of simulated NO_2 columns and those derived from satellite measurements may be helpful, in turn, for evaluation of the satellite measurement derived data, taking into account that the procedure of retrieval of tropospheric NO_2 columns from satellite measurements always involves some a priori assumptions which are difficult to validate, such as the shape of vertical profiles of tropospheric NO_2, or the amount of scattering on aerosols.

The comparison performed within the framework of this study may be especially in-

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teresting from the last point of view particularly because we are the first to compare the latest version (Version 2) of the GOME measurement based data product for tropospheric NO_2 columns from the Bremen University (http://www.doas-bremen.de/) with a CTM which was not used in the stage of retrieval of these data. The main difference between Version 2 and earlier Version 1 data is that Version 2 data were derived using tropospheric NO_2 vertical profiles from the global CTM MOZART (Horowitz et al., 2003) while the constant profile with all NO_2 in a 1.5 km boundary layer was assumed for Version 1 data. That is, on the one hand, it is reasonable to expect that Version 2 data are less uncertain than Version 1 data, but on the other hand, they are more dependent on performance of a certain model (MOZART). Therefore, a comparison of Version 2 data with corresponding data from another model is believed to be a really very useful step for evaluation of that new version of the satellite measurement based data.

This study addresses the following issues. First, we present the newly developed extended version of CHIMERE CTM, which covers the whole Europe and some neighbouring regions, and evaluate its performance over the whole domain. In doing so, we present, up to our knowledge, first comparison of satellite measurement based data for tropospheric NO_2 columns with calculations performed by a continental scale CTM designed to study air quality issues. The advantages of our model over the global CTMs, with which the tropospheric NO_2 columns derived from GOME measurements were compared earlier (Velders et al., 2001; Lauer et al., 2002; Martin et al., 2003; Savage et al., 2004), are higher spatial resolution that matches best the resolution of GOME measurements in the South-to-North direction and more in-detail parameterisation of the boundary layer processes. Our analysis is focused on statistical characterization and comparison of "fine" structure of spatial distributions of the simulated and GOME measurement derived tropospheric fields of NO_2. The comparison of model results with satellite measurement data is supplemented by the comparison of the simulated ground based ozone concentrations with those measured by the EMEP network and two stations of scientific atmospheric monitoring in Russia. On the one hand, the com-

parison of the simulated and observed ground based ozone concentrations allows us to demonstrate that CHIMERE features a sufficiently high level of performance expected for state-of-the-art continental scale models. And on the other hand, it is important in view of possible future applications of CHIMERE to study photo-oxidant pollution in Eastern Europe.

Second, we estimate the upper limits of spatially average random uncertainties (distinctive from systematic uncertainties equally applicable to all pixel considered) for both NO_2 columns simulated by CHIMERE and those derived from GOME measurements. Moreover, we make an attempt to characterise these uncertainties in terms of absolute (additive) and relative (multiplicative) errors. This issue seems to be especially important from the point of view possible application of satellite measurements for inverse modelling of emissions, because simulated NO_2 columns are closely linked to NO_x emission data.

Finally, we pay special attention to the analysis of differences in statistical characteristics and uncertainties of the GOME derived and simulated NO_2 columns between Western and Eastern Europe. Such an analysis is very useful. Indeed, while emissions inventories for Western Europe have been extensively exploited and independently validated in numerous studies comparing results of continental and regional scale CTMs with observations (although in most cases not directly to NO_x or NO_y), the number and extent of similar studies concerning Eastern European countries is incomparably smaller, because of a severe deficit of both models and observations. Recent comparisons of tropospheric NO_2 columns derived from GOME measurements and those calculated by global models did not pay much attention to Eastern Europe, probably because the emission sources there are spread over vast territories, and, correspondingly, the average level of NO_2 pollution is much lower in Eastern Europe than over such densely populated regions as Western Europe or South Asia. Nevertheless, it would be useful to note that, for example, total anthropogenic NO_x emissions in Russia are estimated to be considerably larger than those in any of the Western European countries taken alone (Vestreng, 2003).

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The paper is organized as follows. The brief description of our version of the CHIMERE CTM is given in Sect. 2, and its evaluation with data from the EMEP ground based ozone monitoring network is discussed in Sect. 3. Section 4 provides a description of the methods used to derive data for tropospheric NO_2 columns both from GOME measurements and calculations by CHIMERE. Section 5 is devoted to comparison of the satellite measurement derived tropospheric NO2 columns with the corresponding simulated data, and Section 6 discusses the uncertainties of the analysed data. Finally, results of our study are summarised in Sect. 7.

2. Model description

This study is based on the use of the chemistry transport model CHIMERE which is an Eulerian multi-scale model designed for analysis of various air pollution related issues on urban and continental scales and for routine forecasting air pollution (http://prevair.ineris.fr). Description of basic features of the earlier version of the model can be found in the papers by Schmidt et al. (2001) and Vautard et al. (2001), and important recent updates are presented by Bessagnet et al. (2004). In-detail description of the model, the technical documentation and the source codes are available also on the web (http://euler.lmd.polytechnique.fr/chimere/). Therefore, only those features are mentioned below, which are most important in the context of the given study or specific to our extended version of CHIMERE.

CHIMERE has been thoroughly evaluated both on the urban scale for the Ile-de-France region (Vautard et al., 2001, 2003) and continental scale for Western Europe (Schmidt et al., 2001; Bessagnet et al., 2004). Although CHIMERE enables modelling of both gases and aerosols, this paper focuses on gas-phase processes only.

The continental version of CHIMERE uses a rectangular grid with horizontal resolution of 0.5×0.5°. The new CHIMERE domain used in this study is significantly larger (up to seven times) than any of the domains with which the model was used earlier. Specifically, it covers the region from 15° W to 70° E and from 25° N to 70° N, which

includes the whole Europe, Middle East, and a part of Northern Africa.

Meteorological input data for the CTM have been obtained from simulations with the non-hydrostatic meso-scale model MM5 (http://www.mmm.ucar.edu/mm5/) that has been run on a regular grid with horizontal resolution of 100×100 km. MM5 is initialised and driven with NCEP Re-Analysis data available on the web (http://wesley.ncep.noaa.gov/ncep_data/) with a temporal resolution of 6 h and a spatial resolution varying from 1.8 to 2.5° for different variables. MM5 is employed in order to compensate this too low temporal and spatial resolution of NCEP data. Note that all previous studies with CHIMERE referenced above used ECMWF data with a horizontal resolution of about 50 km. Some "coarsening" of the standard configuration of CHIMERE proved to be inevitable in order to enable efficient simulations for the new larger domain.

In the vertical, the model has 8 layers whose heights are fixed using hybrid coordinates. The top of the upper layer is fixed at 500 hPa pressure level. The fact that CHIMERE does not enable simulations of the most part of the free troposphere presents some limitation for our comparison of model calculations with tropospheric NO_2 columns derived from GOME measurements. However, this issue is not crucial, because, as it is argued in Sect. 5, the spatial variability of tropospheric NO_2 columns is determined mostly by lower tropospheric NO_2. Vertical diffusion is calculated within CHIMERE itself using the parameterisation suggested by Troen and Mahrt (1986). Photolysis rates are calculated using the tabulated outputs from the Troposphere Ultraviolet and Visible model (TUV, Madronich and Flocke, 1998) and depend on altitude and zenith angle. Besides, the attenuation of radiation due to clouds is taken into account, based on the simplified assumption that the processes considered in the model take place below the top of the cloud layer. Correspondingly, the clear sky photolysis rates J_c are scaled with a radiation attenuation coefficient A which is calculated as a function of cloud optical depth; the actual photolysis rates are defined as a product A and J_c.

The chemical scheme used (Derognat, 2002) is the same as the one presented in Schmidt et al. (2001), but with updated reaction rates. It includes 44 species and about

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120 reactions and was derived from the more complete MELCHIOR chemical mechanism (Latuatti, 1997) using the concept of chemical operators (Carter, 1990; Aumont et al., 1997). Lateral boundary conditions are prescribed using monthly average values of the climatological simulations by the second generation MOZART model (Horowitz et al., 2003).

The anthropogenic emissions are prescribed in essentially the same way as in the earlier studies with CHIMERE. Specifically, the annual EMEP data (Vestreng, 2003) for NO_x, SO_2, CO, and non-methane volatile organic compounds (NMVOC) distributed to 11 SNAP sectors and gridded with horizontal resolution of 50×50 km are used to specify emissions of corresponding model species for the most part of the new domain. But because dimensions of the new domain exceed sizes of the EMEP grid, the data from EDGAR V3.2 database (Olivier and Berdowski, 2001) are used to prescribe emissions for some territories (mainly, in Asia). These territories constitute only a minor part of the whole domain and are not the focus of this study. Daily, weekly, and seasonal variations of emissions were prescribed using data provided by the IER, University of Stuttgart (GENEMIS, 1994). As the new domain covers several time zones, the local administrative times were taken into account. The annual NMVOC emissions were splitted first into emissions of 227 real individual hydrocarbons using typical NMVOC profiles (Passant, 2002), and then emissions of these real species were aggregated into emissions of 10 NMVOC model species.

The land use data needed to parameterise biogenic emissions and dry deposition are obtained with a 1 km resolution from the GLCF database (Global Land Cover Facility, Hansen et al., 2000, http://glcf.umiacs.umd.edu) and aggregated to the CHIMERE grid. Biogenic emissions of isoprene, pinene and NO are parameterised in accordance to methodology suggested by Simpson et al. (1999), using distributions of tree species on a country basis provided in their work and the inventory of NO soil emissions by Stohl et al. (1996). The biogenic emissions for African and Asian countries (except Turkey and Kazakhstan) which are not covered in the cited inventories, are not taken into account, because they cannot be adequately described using the above men-

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tioned methodologies designed for temperate regions. Simulations for these countries are anyway not the focus of this study and the paper's conclusions are not affected by this omission.

3. Model evaluation with ground based observations of ozone

3.1. Observational data

While the main aim of this paper is comparison of model results with data derived from satellite measurements, the comparison with ground based measurements presented in this section plays a complimentary role and is intended, mainly, to demonstrate that our version of CHIMERE performs reasonably well in a "classical" way of evaluation of continental scale CTMs. Correspondingly, we do not consider here all available measurement data (that would be hardly possible to do within a single paper anyway), but use only the data of ozone measurements from EMEP ground based monitoring network (http://www.nilu.no/projects/ccc/emepdata.html) for the years 1997 and 2001, and, besides, the data from two Russian ozone monitoring stations situated in remote regions and supervised by Institute of Atmospheric Physics (Moscow). These measurements suit best to our goals, because, on the one hand, predictions of ozone concentration, which, in the real atmosphere, depends on numerous physical and chemical processes, provide indeed a very serious test for the model performance. And on the other hand, as the EMEP network is intended to reflect regional background conditions relatively unaffected by local emissions of ozone precursors, the model resolution should be adequate at least for ozone.

Note that the measurements of other pollutants are less appropriate for comparison with our model. For example, insufficient resolution of the model's grid is the most likely reason for a rather large disagreement between NO_2 monitoring data and continental scale models (see, e.g., Schmidt et al., 2001; Fagerli et al., 2003; Bessagnet et al., 2004). Such disagreement reflects, in particular, the well-known fact of a large spatial

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and temporal variability of that relatively short-lived species. Besides, the measurement and representativeness errors are also considerable in the case of NO_2 (Aas et al., 2000). Consequently, comparison with the ground based measurements of nitrogen dioxide is not discussed in this paper.

The EMEP ozone-measuring network includes about 150 stations. Normally, the hourly continuous measurements are reported. However, for some stations, the data were absent or incomplete for the periods that are considered in our study. Therefore, some selection criteria were needed. Specifically, only these days have been taken into account, for which the number of hourly measurements exceeded 18, and the stations with the data gaps for more than 30% of days in the periods considered have been excluded from the analysis.

As it has been already pointed out in the introduction section, the EMEP monitoring network is extremely sparse over Eastern Europe. Correspondingly, an effort was done to involve relevant data from other sources for this area. Specifically, we used data from ozone measurement stations situated at Kola Peninsula (Lovozero site, 250 m a.s.l., 68.0° N, 35.1° E) and at Russian Caucasian region (Kislovodsk High-Mountain station, 2070 m a.s.l., 43.7° N, 42.7° E). Taking into account that data from only two ozone measuring EMEP stations in Russia are available for the periods considered in this study, the data from even two more ozone monitors provide very substantial additional contribution to available observational information concerning Eastern Europe. Up to our knowledge, no publications are available in which the data from these stations are compared with CTM simulations.

When ground based observations are compared with model results, it is necessary to define which model level corresponds to a given station. The choice of surface layer may be inappropriate for mountain sites where the model's grid cannot resolve details of a relief. In this study, we chose an appropriate model level by considering the difference between the actual height of a site (a.s.l.) and its height in the MM5 model topography (with resolution 100×100 km). Such a procedure is believed to be most unambiguous, although it does not provide a general solution for the problem of low

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resolution of a model in mountainous areas where the performance of the model may be worse than over plains.

3.2. Results

Figure 1 presents a simulated distribution of mean daily maximums of ozone concentrations over model domain in comparison with the corresponding observed data. Note that simulated ozone concentrations are given for the lowest CHIMERE level, and only these stations are shown which, in accordance to the criterion discussed above, correspond to this level. Although it is difficult to judge about adequacy of the simulated ozone distribution based on comparison with the given very fragmentary observational picture, it is useful to note that both observations and measurements manifest the pronounced north-to-south gradient of ozone concentration. Such gradient appears to be quite a reasonable feature of the simulated ozone field taking into account that the stronger insolation and higher temperatures facilitate faster ozone production in densely populated regions in Southern Europe when compared with the similar regions in Northern Europe. Considering variability of ozone concentrations in the West to East direction, it can be noticed that both the model and observation show larger concentration over Germany and Italy than over England, Spain and Portugal in the West and Poland and Slovakia in the East. The high level of simulated ozone concentration over Mediterranean Sea and Persian Gulf is, probably, a result of a combination of large emissions of ozone precursors from surrounding coastal areas, strong radiation, and a low rate of ozone deposition on a water surface. Note also that the mean level of modelled ozone pollution is generally lower over Eastern than Western Europe in agreement with the lower population density and associated emissions of ozone precursors in Eastern Europe. In order to quantify the model performance in capturing spatial structure of the measured mean ozone concentrations, we have evaluated the correlation coefficient between the mean observed and measured ozone concentrations for all sites. It equals 0.70.

Let us further consider several classical statistics used for evaluating air quality mod-

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els. These are the standard correlation coefficient, R, the normalized root mean square error,

$$NRMSE = \frac{\left(\frac{1}{N}\sum_{i=1}^{N}(C_i^m - C_i^o)^2\right)^{1/2}}{\bar{C}^o}, \quad (1)$$

and the mean normalized bias,

$$BIAS = \frac{\bar{C}^m - \bar{C}^o}{\bar{C}^o}. \quad (2)$$

Here, C^o and C^m are observed and modelled daily maximum concentrations at a given location, and $\bar{C}^o$ and $\bar{C}^m$ are their averages over the considered periods.

The statistics for all the measurement sites considered in our analysis are mapped in Fig. 2. The correlation coefficient is higher than 60% for the majority of sites (73 out of 121 considered), and higher than 80% for 15 sites, with an average of 62%. Persistently high correlations are typical for Germany, Belgium, and the Netherlands, and generally smaller ones are found for the sites in Eastern and Northern Europe. This may be indicative of the fact that CHIMERE works best for the sites situated in relatively polluted environments where ozone behaviour is determined by photochemical processes rather than the long-range transport.

However, it is important to note that even when the model performs badly in terms of correlation coefficient, it still may perform quite satisfactory with regard to normalized RMSE. For example, a very small correlation coefficient (29%) and a rather low NRMSE (18%) co-exist for the Kislovodsk high-mountain station. A similar behaviour is observed also for many other remote stations both in North and South of Europe. As the day-to-day variability of ozone concentration is relatively small at these sites, the errors of model predictions, which may be large when compared with the variance of the measured data, look small when compared with the mean value of ozone concentration. Taken on the average for all the sites, the NRMSE is found to be about 24 percents.

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Biases are in the range from −20 to 20 percents for most of the sites. Their absolute magnitudes are less than 10% for 53 out of 121 sites considered, and less than 15% for 84 sites. When averaged over all the sites, the mean bias is slightly positive (about 7 percents).

When comparing model performances for Western and Eastern Europe, it becomes clear that CHIMERE performs better for Western Europe in terms of correlations but that differences are small in terms of NRMSE and mean biases. Specifically, for the sites located to West (East) of 18° E, the average values of the correlation coefficient, the normalised RMSE, and the mean bias are found to be 65, 25, and 6 (44, 22, and 7) percents, respectively. As it has already been noted above, the relatively high correlations are typical for the sites located within highly urbanized regions, which are characteristic of Western Europe rather than of Eastern Europe. Correspondingly, the differences in the model performances with respect to the correlation coefficients cannot be considered as sufficiently strong evidence in favour of better quality of ozone simulations by CHIMERE for Western Europe when compared to those for Eastern Europe. It should be emphasised also that the statistics reported above for Eastern Europe are likely not quite representative of the total Eastern Europe because they are based on the very limited number of stations.

Figure 3 presents examples of simulated and observed time series of ozone daily maximums for several sites in Western Europe and Eastern Europe (Russia). It is interesting to note that the largest differences are observed during the episodes of elevated ozone concentrations, even if they are generally well pronounced in simulations, too. Among the sites presented in Fig. 3, the model performs worst at Lovozero. However, on the one hand, the typical ozone mixing ratio observed in this remote site is very low, and so the absolute errors of model predictions are not very large when compared with the other sites. On the other hand, Lovozero is situated almost on the edge of the model domain and thus the simulated results may depend strongly on the boundary conditions.

The statistics considered above, when taken alone, do not enable conclusions about

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model performance to be drawn in qualitative terms such as “good” or “bad”. Therefore, it would be useful to compare our results with the corresponding results of other European continental scale models. For such a purpose, we consider here the results of model evaluations presented in the Special Report to EUROTRAC (Roemer et al., 2003). Table 1 lists the comparison statistics for daily maximums of ozone concentration, obtained with several continental scale models for different measurements sites. Note that while not all of the sites considered in the Special Report belong to EMEP monitoring network, only EMEP sites are considered here. All the models, including ours, were run for the period from 1 May to 31 August 1997. It seems to be evident that although the performance of our version of CHIMERE is, to some degree, worse than the performance of the “standard” CHIMERE, it still levels, on the average, with the performances of the other models.

Accordingly, considering all the results presented above, we can conclude that our extended version of CHIMERE is a state-of-the-art continental scale model which works satisfactorily in Western, Central, and Northern Europe. However, the available data of ozone measurements do obviously not enable correct evaluation of the model performance for the major part of Eastern Europe, nor for Northern Africa and Middle East, for which no surface observations were available in this work. The comparison of the model results with the data derived from the GOME measurements, which is discussed in the next sections, provides substantial additional information on model performance in Eastern, as well as in Western Europe.

4. Description of tropospheric NO_2 data

4.1. Tropospheric NO_2 columns retrieved from GOME measurements

We use the most recent version (Version 2) of tropospheric NO_2 column data products that were created at the Institute of Environmental Physics (IUP), University of Bremen in the framework of European project POET (http://nadir.nilu.no/poet/). These data

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were derived from the measurements performed by the Global Ozone Monitoring Experiment (GOME) spectrometer on a board of the second European Research Satellite (ERS-2). The GOME instrument is a grating pseudo double monochromator covering the wavelength range from 280 to 790 nm with the spectral resolution of 0.2–0.4 nm (Burrows et al., 1999); it is designed to detect radiation reflected from the ground and scattered back by the atmosphere, as well as the extraterrestrial solar radiance. Although the main target of GOME is observation of ozone fields, its data are used also to retrieve the column amounts of some other gases, including NO_2, by means of the Differential Optical Absorption Spectroscopy (DOAS) method (Richter, 1997, see also http://www.doas-bremen.de/). ERS-2 has a sun-synchronous near-polar orbit with an equator crossing time of 10:30 LT in the descending node. The typical ground pixel size is 320 km across the track (i.e., in West-East direction), and 40 km along the track. The nearly global coverage is reached in 3 days.

It is important to note that the information provided by GOME measurements is sufficient for retrieval of only total atmospheric NO_2 slant columns. In earlier version (Version 1) of data products of the Bremen University group, the tropospheric NO_2 columns were evaluated further using the tropospheric excess method introduced by Richter and Burrows (2002). That method was based on the estimation of stratospheric NO_2 slant columns using total atmospheric NO_2 columns in remote parts of the oceans and the assumption of homogeneity of longitudinal distribution of stratospheric NO_2. In Version 2 data, a longitudinal variability of stratospheric NO_2 is estimated more accurately based on simulations with the global CTM SLIMCAT (Chipperfield et al., 1999) sampled in the time of GOME overpass.

The tropospheric NO_2 columns are then derived from the tropospheric slant columns by applying the pre-calculated air mass factors (AMF) which prescribe an effective path of light in the troposphere and depend, in particular, on vertical distribution of the absorbing gas, aerosol and clouds in the troposphere, and on solar zenith angle and surface albedo. Different approaches and assumptions to evaluate air mass factors were used in different versions of data products of IUP. In particular, Version 1 data

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(see, e.g., Richter and Burrows, 2002; Lauer et al., 2002) were derived under simplified assumptions that all tropospheric NO_2 is homogeneously distributed (in vertical) below 1.5 km. The retrieval of Version 2 data is based on the use of monthly averaged AMF evaluated with NO_2 profiles from the global model MOZART for the year 1997 (Horowitz et al., 2003, see also http://www.mpimet.mpg.de/en/extra/models/mozart/).

Other major improvements concern the evaluations of cloud parameters and surface albedo, which are obtained from GOME measurements using the algorithms discussed by Koelemeijer et al. (2001, 2003). Note that cloud parameters are needed to select the pixels with low cloud cover; a cloud cover threshold equal 0.2 is used in the retrieval of Version 2 data, and no further correction of AMF due to clouds is performed. Version 1 data will not be further discussed in this paper, although it seems worthwhile to note that the comparison of NO_2 columns simulated with CHIMERE with these data were also performed in the preliminary stage of our study. A disagreement between model results and Version 1 data was found to be significantly larger than in the case with Version 2 data that may be indicative of larger uncertainty of Version 1 data.

4.2. Simulated NO_2 columns

We use the model data corresponding to summer seasons of 1997 and 2001. The choice of the year 1997 has been almost obvious, taking into account that evaluation of AMF used for the retrieval of tropospheric NO_2 columns from GOME measurements were based on MOZART run for this year and, consequently, the respective GOME data are expected to be more consistent than the data for any other year. The year 2001 is considered mainly in order to get an idea of a degree to which our estimations may be sensitive to inter-annual variability of tropospheric NO_2. The choice of summer months has been pre-determined by the fact that CHIMERE is designed, primarily, for simulating photo-oxidant pollution that is usually strongest during the warm season. Besides, the uncertainty of GOME data may be larger for other seasons due to larger cloud cover and possible strong reflection from ice and snow.

In order to be consistent with GOME derived data, the modelled NO_2 columns for

each model grid cell are taken in local solar time between 10 and 11 h and only on days with insignificant cloud cover. Because the total cloud cover is not considered in CHIMERE, we use a selection criteria based on a 0.7 threshold value of the radiation attenuation coefficient, which corresponds to 30% reduction of solar radiation due to clouds. We tested the sensitivity of simulated monthly average NO_2 columns to the radiation attenuation coefficient threshold value and found that it is very insignificant. Note also, that whatever a criterion was used, the selection of "good" days and pixels out from the simulated data could not be done quite consistently with the procedure employed for retrieval of GOME data because of the use of different meteorological data.

The daily data for simulated NO_2 columns are combined in order to obtain monthly averaged distributions that can be used for comparison with the data-products for monthly mean NO_2 columns derived from GOME measurements. Besides, in order to provide better similarity of horizontal resolution of simulated and GOME derived data, CHIMERE data has been preliminary averaged for each 7 consecutive grid cells in West-East direction. Note that CHIMERE grid used in this study is exactly the same as the grid used in Version 2 NO_2 data-products. Note also that although our version of CHIMERE is capable to simulate only lower tropospheric NO_2 columns (up to 500 hPa pressure level), we use evaluations of tropospheric NO_2 columns above 500 hPa, obtained using the same output database of the global CTM MOZART that is used to prescribe boundary and initial conditions for CHIMERE (see Sect. 2).

5. Overview and comparison of GOME retrieved and simulated NO_2 distributions over the model domain

Figure 4 presents distributions of tropospheric NO_2 columns derived from GOME measurements, lower and upper tropospheric NO_2 column amounts simulated with CHIMERE (below 500 hPa) and MOZART (above 500 hPa), respectively, and combined (CHIMERE plus MOZART) total tropospheric NO_2 columns; all the data shown are av-

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erages of June to August monthly means. Seasonally averaged distributions rather than data for individual months not only enable more concise presentation and discussion of our results, but it is also very reasonable to consider them from the point of view of potential applications of our results for inverse modelling of emissions. Indeed, averaging of modelled and observational data over summer period enables a drastic reduction of the "random" errors of the data, and, consequently, obtaining more consistent relationships between emission fields and NO_2 columns. Note that the data from MOZART are not quite consistent with the other data considered here, particularly because they correspond to another year. Therefore, we use these data for qualitative characterization of possible contribution of the upper tropospheric NO_2, rather than for exact quantitative estimations.

It is seen in Fig. 4 that many similarities exist between GOME measurements and simulated lower and total tropospheric NO_2 columns. In particular, both kinds of data exhibit the strongly enhanced NO_2 columns over the Great Britain, Belgium, Netherlands, and North-western Germany; some other polluted areas, such as Po Valley in Italy and Moscow region in Russia, are well pronounced. Both CHIMERE and GOME data indicate much lower level of air pollution in Eastern Europe compared to Western Europe. However, along with similarities, there are a number of differences. For example, GOME measurements give significantly larger values of NO_2 columns over Israel and Persian Gulf region than predicted by the models, but the reverse situation is observed, in particular, over areas at Southern Poland and around Moscow.

It is very important to note that, as evidenced by the MOZART data, the contribution of upper tropospheric NO_2 to the total tropospheric NO_2 columns is rather small over the most part of Western Europe. The relative contribution of the upper troposphere is more significant over Eastern Europe; nevertheless, as it can be seen in Fig. 4, spatial variations of both NO_2 columns derived from GOME measurement and those simulated by CHIMERE are generally much stronger than spatial variations of the upper tropospheric NO_2.

Figure 5 presents distributions of NO_2 columns derived from GOME and simulated

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by CHIMERE for summer of 2001. A comparison of Figs. 4 and 5 indicates that inter-annual variability of NO_2 columns is not large, although it can hardly be neglected completely. More careful examination of differences between 1997 and 2001 in the modelled and GOME measurement derived NO_2 columns reveals that they correlate very badly ($R<0.2$) and that the average (over the hole model domain) decrease of NO_2 column amounts is much larger in the CHIMERE (11%) than in the GOME data (0.1%). The last observation indicates that the EMEP emission database may overestimate an actual reduction of the anthropogenic NO_x emissions. However, this supposition needs further careful analysis that is beyond the scope of this paper.

In order to enable a statistical analysis of differences between Western and Eastern Europe, we define two regions, one of which is restricted between 10° W, 18° E, 35° N and 60° N, and another between 18° E, 65° E, 40° N and 65° N. These regions will be referred to in the following as to Western and Eastern Europe, respectively. Although such a definition does not follow exactly any political boundaries, nevertheless, such defined regions seem to be well representative of more densely populated industrial regions in Western and Central Europe on the one hand, and less urbanized countries in Eastern Europe on the other hand.

Figure 6 presents the scatter-plots of simulated and GOME measurement derived NO_2 columns for Western and Eastern Europe. It is seen that the correlations are rather significant, although the scatter is also substantial. The agreement is apparently better for Western Europe; however, it is necessary to take into account the differences in scales of variability of the data for the two regions. The better correlations for Western Europe may stem simply from the fact that the range of possible magnitudes of NO_2 columns at Western Europe is much larger when compared to Eastern Europe. The differences between the considered regions are discussed in more details in the next section.

It is noteworthy that the slopes of the linear fits are considerably less than unity in all cases shown in Fig. 6. It is indicative of significant systematic errors in, at least, one of the considered datasets, whose magnitudes are dependent on the amplitude of the

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NO_2 columns. It is interesting to note also that a few points corresponding to values above $3{\cdot}10^{15}$ mol/cm^2 in Eastern Europe look as if they were outliers, especially in the case of 1997. They correspond to the areas about Krakow in Poland and Moscow in Russia. This observation may be indicative of overestimated NO_x emissions prescribed in CHIMERE for these two areas. This overestimation is, probably, much stronger in the EMEP emission database for 1997 than for 2001.

Table 2 lists the basic statistical characteristics of the discussed data for different months and years. Estimates of contributions of upper tropospheric NO_2 are given in Table 3. It is easy to see that the means of CHIMERE and GOME data agree for Western Europe within less than 32% of uncertainty (relative to the mean of the GOME retrievals) for all months considered in 1997. The negative difference between the means of the CHIMERE and GOME NO_2 columns is larger in 2001 and reaches 41% in August. The larger difference in 2001 is, mainly, due to the reduction of NO_2 column amounts in CHIMERE data in that year (compared to 1997), which is not found in GOME data. The consideration of the results given in Table 2 together with the estimates provided in Table 3 reveals that a considerable part of the noted discrepancies can be explained by the unaccounted contribution of the upper tropospheric NO_2 in CHIMERE NO_2 columns. But even without account of the upper troposphere, the obtained agreement between the model and GOME seems to be rather satisfactory. Indeed, the strong positive difference (more than 150% for Western Europe in summer months) between simulations performed with a global CTM and Version 1 GOME measurement derived data has been found by Lauer et al. (2002). Savage et al. (2004) have also found a strong positive difference (about 120%) between their simulations and GOME retrievals in June of 1997, although smaller differences (about 60%) have been found in July and August. Note, however, that Savage et al. compare their simulations with the GOME retrievals that are based on the same modelled NO_2 vertical profiles that have been used to calculate the modelled NO_2 columns, while the vertical NO_2 profiles that have been used to elaborate Version 2 data-products considered here are different from those obtained from CHIMERE. In our case, there is there-

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fore a greater chance that systematic errors of the modelled and GOME measurement derived NO_2 columns have the same sign and similar magnitude. Nonetheless, an important advantage of our approach is that the random errors of the NO_2 columns from CHIMERE and GOME can be assumed to be statistically independent. This advantage is exploited in the next section.

As to Eastern Europe, CHIMERE gives about a factor two lower mean values than those derived from GOME measurements. However, it is easy to see that accounting for a contribution of the upper troposphere would again enable considerable improvement.

As it was already discussed above and is evidenced by the results presented in Tables 2 and 3, an expected contribution of the upper troposphere to variability of the total tropospheric NO_2 columns is rather small for both Western and Eastern Europe. Thus, the standard deviations (σ) of the data derived from GOME measurements and simulated with CHIMERE are compared directly. It is seen that the standard deviations of the seasonally averaged data agree within less than 20% of uncertainty for both years in Western Europe. But the differences are larger in monthly data, especially in August of both 1997 and 2001. In Eastern Europe, the difference is especially strong in 2001. It is particularly noteworthy that NO_2 columns from GOME show persistently stronger spatial variability than those from CHIMERE.

The disagreement of the standard deviations is not easy to interpret unambiguously because they bear information not only on variability of "true" values of the analysed characteristics and a contribution of random errors, but also on systematic errors that covariate with the true values. For example, our situation with the larger standard deviations of GOME data than that of CHIMERE data could be explained by larger random errors (noise) in the data from GOME. But on the other hand, we could expect the similar result if the data from GOME or CHIMERE were scaled with a nearly constant factors that are less or greater than unity, respectively. Those factors would represent systematic multiplicative (geometric) errors of the respective data.

The potential sources of systematic errors in NO_2 columns from a CTM and GOME

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are quite numerous and have already been discussed in details by Savage et al. (2004) and Boersma et al. (2004). It is important that the most likely errors both in models and in the GOME retrieval procedure are indeed of a multiplicative character, as they are associated, on the one hand, with miscalculation of NO_2 lifetime (due to errors in vertical transport, chemistry and deposition) and, on the other hand, with uncertainties of the air mass factor (due, e.g., systematic errors in input vertical profiles of tropospheric NO_2 or scattering on aerosols).

Regarding the differences in statistics for Western and Eastern Europe, it is useful to note that while values of both the mean and the standard deviation are significantly smaller for Eastern Europe, the relative differences are much larger in the standard deviations than in the means. Consequently, the ratios of the standard deviation to the means of both GOME derived and simulated data for Western Europe are considerably larger than the corresponding ratios for Eastern Europe. Specifically, these ratios are 37% and 75% higher for Western than for Eastern Europe in the case of CHIMERE data for 1997 and 2001, respectively. The differences are even much larger with the GOME data, because of more significant contribution of the free tropospheric NO_2 to GOME data over Eastern Europe. These results mean, in particular, that if values of NO_2 columns for Eastern Europe were linearly scaled to obtain the same means for the both regions, the variance of such scaled values for Eastern Europe would be considerably less than that of the data for Western Europe. This substantial difference in distributions of NO_2 columns over Western and Eastern Europe seriously hinders the direct comparison of their uncertainties. In particular, in such a situation the smaller coefficient of correlation for Eastern Europe than for Western Europe can be explained not only by larger uncertainty of the data for Eastern Europe but by less variability of "true" NO_2 columns as well.

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6. Analysis of "random" (non-systematic) uncertainties of modelled and GOME measurement derived distributions of tropospheric NO_2

6.1. Evaluation of the upper limit for the uncertainties

Let us consider the following variance of the difference,

$$\mathrm{E} = \frac{1}{N}\sum_{i=1}^{N}\left(z_g^i - z_c^i - \bar{z}_g + \bar{z}_c\right)^2, \quad (3)$$

where z_g^i and z_c^i are values of NO_2 columns derived from GOME measurements and those simulated by CHIMERE for an i-th grid cell, respectively, while $\bar{z}_g$ and $\bar{z}_c$are their mean values.

The meaning of E becomes easier to interpret if we write the following formal equalities,

$$z_g^i = z_t^i + \varepsilon_g^i + \Delta_g,$$
$$z_c^i = z_t^i + \varepsilon_c^i + \Delta_c, \quad (4)$$

where z_t^i is a true (unknown) value of tropospheric NO_2 column, ε_g^i and ε_c^i are random errors (with the zero means) of GOME derived and simulated NO_2 columns, and

$$\Delta_{g,c} = \frac{1}{N}\sum_{i=1}^{N}\left(z_{g,c}^i - z_t^i\right) \quad (5)$$

are the systematic part of errors.

After substitution Eq. (4) into Eq. (3), E is expressed as follows,

$$\mathrm{E} = \frac{1}{N}\sum_{i=1}^{N}\left(\varepsilon_g^i - \varepsilon_c^i\right)^2 \quad (6)$$

That is, E is simply the mean squared difference of "random" (non-systematic) errors. If we assume further that these errors are almost independent, that is,

$$\overline{\varepsilon_g \varepsilon_c} \ll \overline{\varepsilon_{g,c}^2}, \quad (7)$$

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then we find that

$$E \cong \overline{\varepsilon_g^2} + \overline{\varepsilon_c^2}. \quad (8)$$

So, under the given assumption, E represents the total mean squared error associated with both GOME derived and simulated NO_2 columns. In other words, the evaluation of E allows us to estimate the upper limit of random component of the uncertainty of either of the two datasets considered. The assumption (7) seems to be very reasonable considering the principal differences in methods used to obtain the data that we compare. Even if a strong covariance existed between uncertainties of NO_2 columns simulated by CHIMERE and MOZART, it could cause much smaller covariance between uncertainties of NO_2 columns simulated by CHIMERE and those derived from GOME, because the latter are sensitive to vertical profiles of NO_2 rather than to their column amounts. Possible reasons for a non-zero covariance between the uncertainties of CHIMERE and MOZART might be the use of MOZART data for prescribing boundary conditions for CHIMERE and correlations of errors of anthropogenic emissions prescribed in the models. But it seems very unlikely that this covariance may be strong, taking into account that CHIMERE and MOZART use different chemical schemes, different gridded emission databases (EMEP and EDGAR, respectively), meteorological data, and, besides, have very different horizontal resolution.

The squared roots of E (that is, RMSE with respect to random errors) and their normalized values are listed in Table 4. It is seen that the errors are rather significant for both regions, and that they are larger when compared with the standard deviations than with the means of GOME derived data, especially for Eastern Europe. The last observation means that variations of the NO_2 columns in space are more uncertain than their absolute values. The uncertainties of the data averaged over three months are less than the uncertainties of the monthly datasets, but it is easy to see that their reductions are smaller than it could be expected if the errors for different months were independent (that is, the reductions are smaller than the square root of 3). Hence, we can conclude that there is a long-term autocorrelation in the errors, i.e., that a

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significant part of the error is persistent beyond the monthly time scale.

It is noteworthy that while the ratios of RMSE to the mean are larger for Western Europe, the ratios of RMSE to the standard deviation are much larger for Eastern Europe. Therefore, based on these results it seems impossible to conclude unambiguously whether the agreement between simulated and GOME derived data is better for one or the other part of Europe. The reason has already been discussed in the previous section. Nevertheless, as it is shown below, the picture will become clearer when analysing uncertainties as a function of magnitudes of the NO_2 columns.

6.2. The random error as a function of amplitude of NO_2 columns

As a preliminary step to further analysis, we would like to introduce the following simplified model of errors. Let us x_m and x_t be measured (or, simulated) and true values of the characteristic x, which are related to each other as follows:

$$x_m = x_t(\delta_s + \delta_r) + \Delta_s + \Delta_r, \quad (9)$$

where δ_s, δ_r, Δ_s, and Δ_r are systematic and random parts of multiplicative and additive errors, respectively. It is assumed that δ_s and Δ_s are constants, while δ_r and Δ_r are random variables independent of x_m. Such assumptions are hardly satisfied exactly in any real situation, but they still may be a reasonable and useful approximation. We further apply this model to our case in order to try to estimate multiplicative and absolute errors independently.

Figure 7 presents the dependences of "running" evaluations of $E^{1/2}$ (see Eq. 3), as a function of corresponding running averages of the GOME or CHIMERE NO_2 columns for Western Europe. The running averages and statistics were calculated using a window consisting of 100 consecutive data points after the arrangement of all pixels in a growing order (with respect of GOME derived or simulated NO_2 columns). Such a window was chosen as a reasonable compromise between poorer statistics and higher resolution that could be obtained with a narrower window and richer statistics but lower resolution with a wider window. We have found, however, that even the use of very

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different windows (covering, for example, 50 or 200 points) would not lead to serious changes in our results.

It is seen that along with random fluctuations, there is a well-pronounced quasi-linear positive trend in magnitudes of uncertainties. The largest deviation from the linear law takes place for the biggest NO_2 columns in the case of the dependencies on the running averages of CHIMERE data. This exception concerns, however, only a small part (less than 8%) of the total number of data points. It is noteworthy that the slopes of the best linear fits are significantly different in the cases of CHIMERE and GOME data.

In order to interpret these results, we have transformed the data from CHIMERE and GOME for 1997 by adding to them artificial systematic and random multiplicative errors and have analysed them in the same way as described above. Specifically, in the case of GOME data, we have applied a systematic multiplicative error factor δ_s=0.75, in accordance to a slope of the corresponding best linear fit in Fig. 6, and random multiplicative errors δ_r with a standard deviation of σ_r=0.22, in accordance to the slope of the corresponding fit in Fig. 7. In the case of the CHIMERE data, we have used δ_s=1.33 (0.75^{-1}), and σ_r=0.22. The random errors have been sampled from the lognormal distribution. The results of the analysis of such artificial errors are presented in Fig. 8.

The slopes of the linear fits shown in Fig. 8 are very close to those shown in Fig. 7. Thus we can conclude that the behaviour of the curves shown in Fig. 7 can be mainly explained by the presence of systematic and random multiplicative errors. It is impossible, however, to determine which of the datasets contains more errors. Most probably, both CHIMERE and GOME data contain both systematic and random errors. Nevertheless, our analysis allows us to evaluate the upper limits of the relation of the standard deviation of the multiplicative random errors (σ_r) to the factor of the systematic multiplicative error (δ_s) as the magnitudes of the slopes of the best linear fits shown in Fig. 7. The same magnitudes, evidently, give an estimate of the random part of the mean relative error, as the latter represents (by the common definition) the mean ratio of an absolute error to the measured (or theoretically specified) value of the quantity

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considered, rather than to the unknown true value.

Certainly, our estimates are not quite exact, but it is hardly possible to put statistically correct constraints to them, particularly because the real data do not satisfy exactly to the simplified model (9) with known distributions of random errors. However, taking into account that both CHIMERE and GOME data are not quite perfect and that their partial errors are therefore significantly smaller than the total errors, and considering the deviations of the analysed quantities from the linear fits, it seems to be safe to conclude that the random part of the mean relative error of NO_2 columns from CHIMERE and GOME for Western Europe is, on the average, certainly less than 35 and 25 percents, respectively. The contribution of the additive errors is not well pronounced, but they are, on the average, evidently less than $3{\cdot}10^{14}$ mol/cm^2.

Figure 9 presents the results of similar analysis for Eastern Europe. In order to facilitate a comparison between the results for Western and Eastern Europe, this figure reproduces also the fragments of the corresponding dependences for Western Europe. The most surprising result is that the uncertainties for Eastern Europe are substantially lower than the uncertainties for Western Europe for the major part of the range of magnitudes of NO_2 columns for Eastern Europe, especially when the uncertainties are considered versus the data from GOME. Indeed, it seemed to be reasonable to expect that the potential uncertainties of input information used in CHIMERE and for retrieval of GOME NO_2 columns are larger for Eastern Europe than for Western Europe. Probably, this result is, mainly, due to the fact that Western European regions with relatively low level of NO_2 pollution are situated usually in vicinity of much more polluted regions, whereas for Eastern Europe they are more homogeneous and wide spread. As a consequence, the uncertainties of the NO_2 transport simulated by CHIMERE, on the one hand, and a low resolution of MOZART data used to evaluate AMF, on the other hand, may play much more significant role under considered conditions in Western Europe than in Eastern Europe.

It is evident that the uncertainties for Eastern Europe have more complex character than those for Western Europe with a less clear correlation between uncertainties and

absolute NO_2 columns. However, they also demonstrate positive trends with the increase of the magnitudes of NO_2 columns, which are indicative of multiplicative errors. The slopes of the linear fits give estimates of the upper limit of the mean relative (multiplicative) error of the respective data, and the origin of the fits on the axis of ordinates give estimates of mean additive error. The latter is obviously less than $2{\cdot}10^{14}$ mol·cm^{-2} in all cases considered. However, the considerable scattering of the fitted uncertainties indicates that the actual errors of the NO_2 column in a given pixel may be considerably different from the mean values estimated here. Therefore, these estimates should be used with care.

The analysis with a running window has been repeated for each of the summer months of 1997 and 2001, and corresponding estimations of the relative errors are listed in Table 5. As it could be expected, the errors of the monthly mean data are, on the average, larger than the errors of the seasonally averaged datasets. The monthly estimates are rather divergent, but have some common features in different years. For example, the difference between the estimates for CHIMERE and GOME data are largest for Western and Eastern Europe in August of both 1997 and 2001. This and some other similarities between our results for 1997 and 2001 may be due to some regular differences in quality of the data from CHIMERE and GOME in different months of a year.

6.3. Discussion

We now discuss results obtained in the previous section in relation to independent estimates of uncertainties of tropospheric NO_2 columns derived from GOME measurement and those simulated by the models. As pointed out before, the multiplicative and additive errors defined above represent upper limits of random errors both in the GOME derived and simulated NO_2 column.

The main sources of errors in the GOME NO_2 columns are (i) the fit of NO_2 column from the spectrum, (ii) separation of stratospheric and tropospheric NO_2, and (iii) evaluation of tropospheric light path (including uncertainties associated with the

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surface albedo, AMFs, and cloud effects). For the Bremen V1 dataset, Richter and Burrows (2002) estimated the random (both in time and space) uncertainties associated with each individual NO_2 fit to be in the range of 2–4·10^{14} mol/cm^2. Obviously, the random uncertainties are significantly smaller (up to a factor of 3) in monthly averages of the retrieved data and, therefore, they can hardly contribute significantly to discrepancies between the simulations and GOME retrievals in our case. The upper limit for uncertainties associated with separation of stratospheric and tropospheric slant columns was estimated to be also about 10^{15}, and is, probably, much lower in case of Version 2 data as result of the use of the SLIMCAT output and the restriction to summer months. Finally, the uncertainties of Version 1 data, associated with the evaluation of tropospheric light path have been estimated to be in the wide range of ±200%. The tropospheric light path is evaluated much more consistently in Version 2 data and, also restriction to summer months reduces problems with clouds, snow and low sun. Therefore, it is reasonable to expect that the corresponding uncertainties should be significantly lower than 200%, as evidenced also by our results.

Martin et al. (2003) have reported estimates for uncertainties of their own version of data for tropospheric NO_2 columns derived from GOME measurements. Specifically, they estimated the absolute error of their data to be about 10^{15} mol/cm^2 and derived the total relative error to be of 42% for each scene and suggested that the monthly mean errors can be up to a factor of five less. Similar to Version 2 data used in our study, the data by Martin et al. are based on AMF factors evaluated with data from a global CTM. However, along with this and some other similarities, there are also some methodological differences, which might lead to some differences in uncertainties of the retrieved data.

Boersma et al. (2004) have recently published a detailed error analysis of their GOME NO2 product and discussed the impact of different error sources on the final product. Although the exact numbers depend strongly on the location, season and assumptions made, they give relative uncertainties of 35–60% over polluted regions such as Western Europe and a lower limit for detectable columns of 3·10^{14} mol/cm^2.

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Again, the retrieval method used in this study differs from that of Boersma et al. (2004) in several points, but the overall errors should be comparable.

While the independent estimations discussed above concern the total mean relative error (which includes both systematic and random multiplicative errors), we have estimated here only its random (in space) part. Besides, our estimations include the unknown contribution of errors of NO_2 columns from CHIMERE. Meanwhile, it seems reasonable to expect that the systematic part of the errors of GOME data is not larger than their random part, because a contribution of different sources of errors may strongly vary in space. If it is so, the total mean (RMS) relative error of the Version 2 Bremen dataset for Western Europe is less than 50%, and the total mean additive error is less than $3 \cdot 10^{14}$ mol/cm^2. Such limits are consistent with the independent estimates discussed above. Note that estimations of the random part of the errors of the GOME data (in contrast to estimations of total errors that include both systematic and random parts) can be especially useful for their potential applications to inverse modelling of emissions, as the standard methods of inverse modelling usually require a priori specification of the probability distribution function for errors of observations (see, e.g., Enting, 2002).

Although independent direct estimates of the uncertainty of NO_2 columns simulated by CHIMERE are not yet available, it seems reasonable to assume that it cannot be much lower than the uncertainty of the employed NO_x emission data. The uncertainty of available emission data is, most probably, in the range from 20 to 40 percents for Western Europe (see, e.g., Hanna et al., 1998; Kühlwein and Friedrich, 2000; Kühlwein et al., 2002; Beekmann and Derognat, 2003), but essentially unknown for Eastern Europe. Our estimations for the upper limit of the mean relative errors of the simulated NO_2 columns averaged over summer months (32% for Western Europe and 24% for Eastern Europe) is in line with common understanding of uncertainty of emission data. Note that it would be inappropriate to conclude that the uncertainty of emission data is greater for Western Europe than for Eastern Europe, since the difference in our estimates for Western and Eastern Europe may be due to the difference in the uncertainty

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of the GOME data.

7. Summary and conclusions

The main objectives of this study were (i) evaluation of the newly developed extended version of the CHIMERE CTM over its new large domain with a particular focus on Eastern Europe and (ii) evaluation of the new version (Version 2) data-products for tropospheric NO_2 column amounts derived from GOME measurement over Europe. In order to achieve these objectives, we have first compared the daily maxima of ground ozone concentrations simulated by CHIMERE for summer months of 1997 and 2001 with the corresponding data of ground based ozone measurements performed at more than 100 sites situated, mainly, in Western and Central Europe. We have found, in particular, that the average (over all the station considered) values of the correlation coefficient, the normalised RMSE, and the mean relative bias for daily maximums of ozone concentrations in 2001 are about 62, 24, and 7 percents, respectively. Values of the correlation coefficient are lower for available Eastern European sites when compared to those for Western European sites (44% versus 65%, on average), but, the biases and the normalised RMSE are higher (although very insignificantly) for Western European sites (6% versus 7%, and 22% versus 25% on the average, respectively). It has been argued that differences in correlation coefficients may be, in part, attributed to differences in environments of typical sites in Western and Eastern Europe. These results allow us to make a tentative conclusion that the overall model performance with regard to simulations of ground ozone is similar both for Eastern and Western Europe. However, this conclusion is indeed tentative because of severe deficit of ozone measurement data for Eastern Europe. On the whole, the results of the comparison of the simulated and observed ozone concentrations show that CHIMERE demonstrates a rather satisfactory performance similar to or better than other state-of-the-art European continental scale models.

We have compared next the tropospheric NO_2 columns derived from GOME mea-

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surements and NO_2 column amounts calculated by CHIMERE. Specifically, we have considered the summer seasons of 1997 and 2001, and the main attention has been paid to the seasonally average spatial distributions of the tropospheric NO_2 columns. Because the model enables simulations only in the lower troposphere (below 500 hPa pressure level), the focus of our analysis was put on spatial variability of tropospheric NO_2 columns, as, indeed, the upper tropospheric part, as simulated with MOZART model, shows only little spatial variability.

The consideration of spatial correlations between the gridded data for measured and simulated NO_2 columns has revealed a rather close agreement between them over Western Europe, where correlation coefficients for seasonally average data are found to be equal to 0.91 in 1997 and 0.89 in 2001. For Eastern Europe, the correlation coefficients are smaller (0.76 and 0.80 in 1997 and 2001, respectively). However, it is argued that a conclusion about relative quality of the data for Western and Eastern Europe based on correlation and other standard comparison statistics may be misleading because of the considerable difference between statistical distributions of the data for these two regions.

The reasonable assumption of independent error sources for GOME derived and simulated NO_2 columns has allowed us to estimate the upper limits of such errors. It has been found, in particular, that maximum RMSE of both simulated and measurement based NO_2 columns for summer seasons of 1997 and 2001 constitutes less than 38% of the corresponding mean values of tropospheric NO_2 columns derived from GOME measurements for Western Europe, and less than 30% for Eastern Europe.

Finally, we have considered the dependences (in statistical sense) of the uncertainty estimations on magnitude of the simulated and GOME measurement derived tropospheric NO_2 columns. We have found that a dominating component of the total errors for Western Europe has a multiplicative character, and the corresponding relative random error of the seasonally averaged GOME NO_2 data has been estimated to be less than 23%. As to Eastern Europe, our results suggest that the additive component of the total uncertainty of the simulated and GOME measurement derived NO_2 columns

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is very substantial (compared to the multiplicative component), especially over less polluted (predominantly rural) regions. The mean relative error is very different in different years (0.15 versus 0.06 in 1997 and 2001, respectively). The most interesting (and even surprising) result is that the agreement between the simulated and measurement based tropospheric NO_2 columns has been found to be generally better over Eastern Europe than over Western Europe for low NO_2 columns. Therefore, in a contrast to our initial expectation, we have found no evidences, that either the performance of CHIMERE or the quality of the NO_2 columns derived from GOME measurements is unambiguously worse for Eastern than for Western Europe.

On the whole, our study demonstrated a rather close agreement between tropospheric NO_2 columns derived from GOME measurements and those modelled by the extended version of CHIMERE. The use of a continental scale model has made possible comparison using the true resolution of the GOME measurement derived data, in contrast to earlier comparisons performed with global models. No doubt, that the use of state-of-the-art continental scale models featuring in relatively high spatial and temporal resolution will be especially advantageous when model results will be considered in parallel with the data retrieved from the satellite instruments of the latest generation, SCIAMAHY and OMI, which provides considerably higher resolution of measurements than the GOME instrument. Given the good agreement in spatial structures displayed both by GOME derived and simulated tropospheric NO_2 columns, and given the expected rather linear relationship between NO_x emissions and NO_2 columns, another interesting perspective of this work is to derive regional scale emissions from satellite data by means of inverse modelling.

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Table 1. Comparison statistics calculated for daily maximums of ozone concentrations observed at EMEP stations and simulated by European scale chemistry transport models for the period from 1 May to 31 August 1997. The results for the standard version of CHIMERE and other models are listed in accordance to Roemer et al. (2003).

		R, %			*NRMSE*, %			*BIAS* (%)		
		chimere[(1)]	chimere[(2)]	other models avg.[(3)]	chimere[(1)]	chimere[(2)]	other models avg.[(3)]	chimere[(1)]	chimere[(2)]	other models avg.[(3.6)]
Vredepeel	nl	84	81	72	20	35	31	20	20	10
Eupen	be	80	80	70	29	29	28	17	13	5
Deuselbach	de	85	84	67	15	18	23	6	2	11
Brotjacklriegel	de	77	81	51	23	12	23	−2	1	14
Payerne	ch	79	68	67	15	29	19	4	18	8
Illmitz	at	68	62	55	14	17	22	−4	0	12
Ispra	it	56	43	39	25	29	33	−13	11	18
Aston hill	uk	64	62	47	49	36	46	39	12	22
Harwell	uk	70	78	66	28	26	32	13	−3	10
Sibton	uk	69	86	60	31	20	33	2	1	12
Yarner wood	uk	68	71	58	33	26	38	23	4	20
Eskdalemuir	uk	71	79	62	42	23	31	33	3	14
Mace Head	ie	68	68	60	15	27	27	2	−15	7
average[(4,6)]		**72**	**73**	**60**	**26**	**25**	**30**	**14**	**8**	**13**
Birkenes	no	51	nd	38	23	nd	27	10	nd	9
Jeløya	no	52	nd	45	19	nd	23	3	nd	10
Rörvik	se	63	nd	47	18	nd	23	10	nd	10
Utö	fi	36	nd	39	18	nd	26	3	nd	14
Vindeln	se	51	nd	42	25	nd	28	2	nd	10
Esrange	se	45	nd	45	23	nd	33	−8	nd	23
Aliartos	gr	20	14	10	20	nd	27	5	nd	12
Noia	es	69	65	44	16	24	31	3	−19	14
San Pablo	es	61	nd	34	14	nd	24	−9	nd	15
Preila	lt	52	44	47	24	21	27	14	6	14
Starina	sk	48	47	36	20	31	25	6	25	6
Kosetice	cs	73	65	52	13	16	24	−2	0	13
K-puszta	hu	−23	−26	−21	31	28	34	−21	−15	25
average[(5,6)]		**46**	**nd**[(7)]	**35**	**20**	**nd**[(7)]	**27**	**7**	**nd**[(7)]	**13**

[(1)]: the current version of CHIMERE, [(2)]: the standard Western European version of CHIMERE participated in the study by Roemer et al. (2003), [(3)]: the average over other European models (NILU-CTM, EUROS, MATCH, LOTOS, EURAD, REM3/CALGRID, DEM, STOCHEM, DNMI) participated in the study by Roemer et al. (2003), [(4)]: average over stations from Vredepeel to Mace Head, [(5)]: average over stations from Birkenes to K-puszta, [(6)]: for biases, the averages over their absolute values are given, [(7)]: not enough data

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Table 2. Basic statistical characteristics of spatial distributions of GOME measurement derived and simulated tropospheric NO_2 columns for Western Europe (WE) and Eastern Europe (EE).

year	period	*mean* (mol×10^{15}/cm^2)				σ (mol×10^{15}/cm^2)				*R*	
		WE		EE		WE		EE		WE	EE
		GOME	CHIMERE	GOME	CHIMERE	GOME	CHIMERE	GOME	CHIMERE		
	June	1.94	1.72	1.20	0.69	1.96	1.67	0.50	0.44	0.80	0.58
	July	2.41	1.84	1.27	0.69	2.00	1.99	0.63	0.54	0.86	0.69
1997	August	2.39	1.64	1.27	0.65	2.35	1.34	0.64	0.45	0.87	0.67
	average	2.25	1.73	1.24	0.68	2.10	1.66	0.59	0.48	0.84	0.65
	summer	**2.26**	**1.75**	**1.25**	**0.68**	**2.00**	**1.66**	**0.51**	**0.47**	**0.91**	**0.76**
	June	1.94	1.51	0.85	0.56	1.78	1.57	0.56	0.34	0.78	0.66
	July	2.39	1.57	1.35	0.66	1.81	1.66	0.60	0.35	0.87	0.76
2001	August	2.44	1.44	1.50	0.58	2.28	1.30	0.82	0.34	0.87	0.68
	average	2.25	1.50	1.23	0.60	1.95	1.51	0.58	0.34	0.84	0.70
	summer	**2.26**	**1.51**	**1.24**	**0.60**	**1.85**	**1.50**	**0.58**	**0.34**	**0.89**	**0.80**

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Table 3. Statistical characteristics of upper tropospheric (below 500 hPa pressure level) NO_2 columns estimated using MOZART output database.

period	*mean* (mol×10^{15}/cm^2)		σ (mol×10^{15}/cm^2)	
	WE	EE	WE	EE
June	0.48	0.57	0.07	0.06
July	0.51	0.56	0.10	0.08
August	0.55	0.55	0.14	0.09
average	0.51	0.56	0.10	0.08
summer	**0.51**	**0.56**	**0.10**	**0.07**

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Table 4. Statistics for the total random errors of tropospheric NO_2 columns derived from GOME measurements and those calculated by CHIMERE.

year	period	*RMSE* (mol×10^{15}/cm^2)		$\frac{RMSE}{mean[gome]}$		$\frac{RMSE}{sigma[gome]}$	
		WE	EE	WE	EE	WE	EE
1997	June	1.19	0.44	0.61	0.36	0.61	0.87
	July	1.05	0.47	0.43	0.37	0.52	0.75
	August	1.34	0.47	0.56	0.37	0.57	0.74
	average	1.19	0.46	0.53	0.37	0.57	0.79
	summer	**0.85**	**0.34**	**0.38**	**0.28**	**0.43**	**0.67**
2001	June	1.13	0.43	0.58	0.50	0.64	0.75
	July	0.89	0.41	0.37	0.30	0.49	0.68
	August	1.31	0.64	0.54	0.43	0.57	0.78
	average	1.11	0.49	0.50	0.41	0.57	0.74
	summer	**0.84**	**0.37**	**0.38**	**0.30**	**0.46**	**0.64**

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Table 5. Estimations of the upper limits of the mean random relative (multiplicative) error (%) of tropospheric NO_2 columns retrieved from GOME measurements and those calculated by CHIMERE.

year	period	WE		EE	
		GOME	CHIMERE	GOME	CHIMERE
1997	June	33	49	14	30
	July	36	29	26	28
	August	17	59	19	37
	average	29	46	20	32
	summer	**22**	**32**	**15**	**24**
2001	June	31	39	10	14
	July	26	30	7	21
	August	16	52	7	41
	average	24	40	11	25
	summer	**23**	**32**	**6**	**24**

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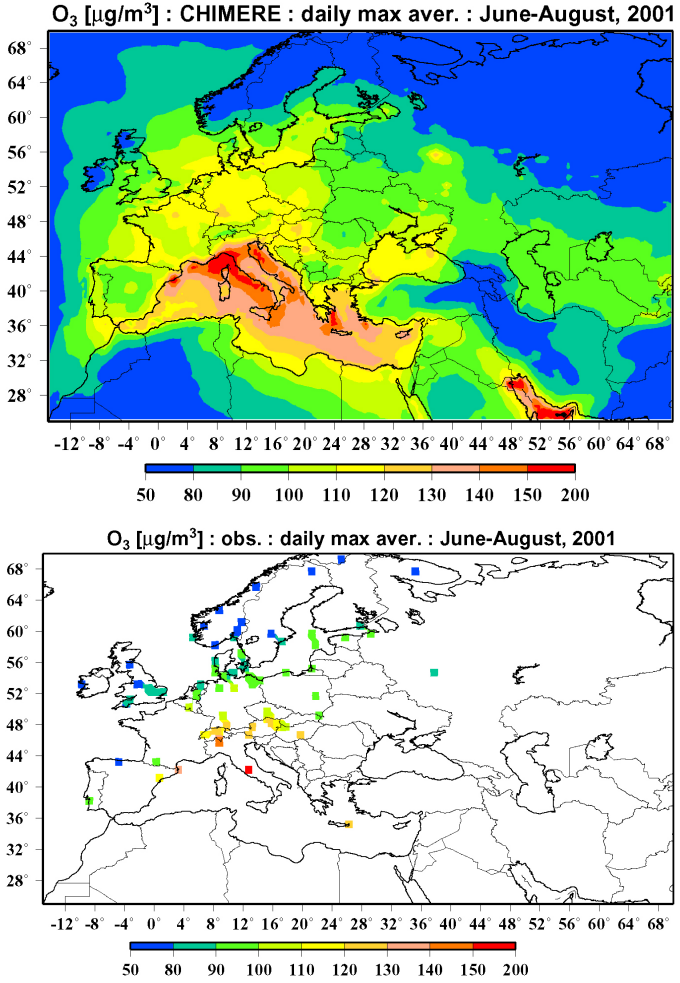

Fig. 1. Spatial distributions of daily maximum average ozone concentrations calculated by CHIMERE and observed at stations of the EMEP monitoring network.

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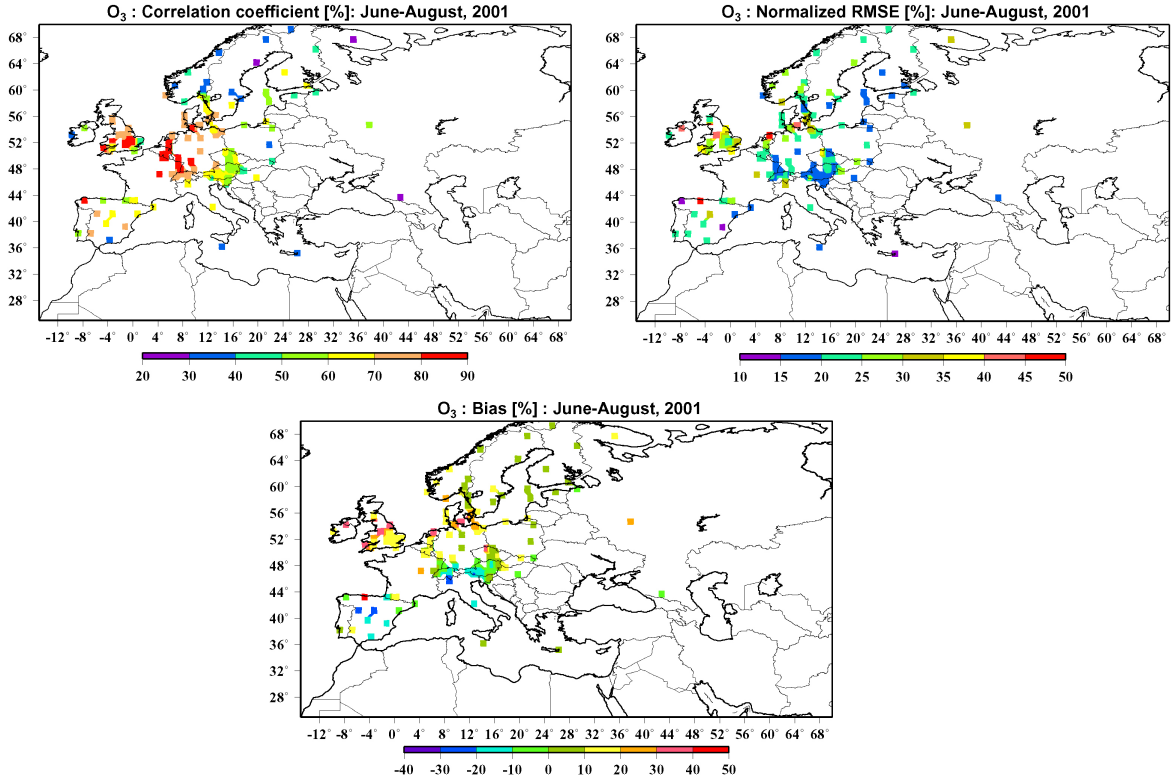

Fig. 2. Comparison statistics for daily maximums of ozone concentrations simulated by CHIMERE and measured by ground based ozone monitors.

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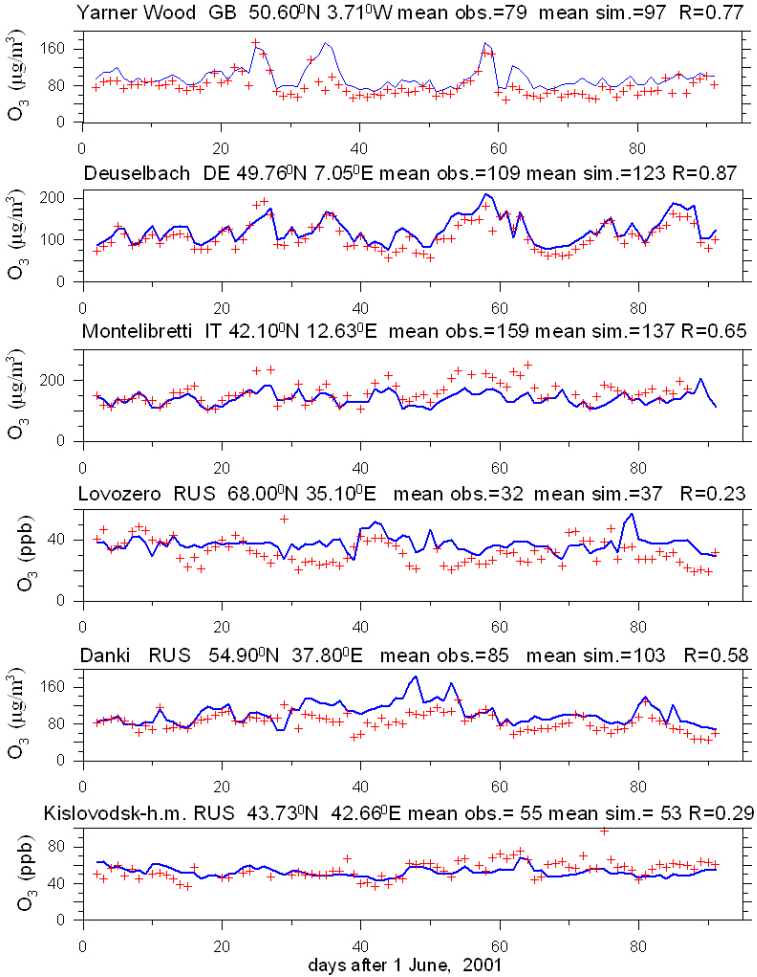

Fig. 3. Time series of daily maximums of ozone concentrations (mixing ratios) for summer season 2001. Solid lines and crosses show model results and observations, respectively.

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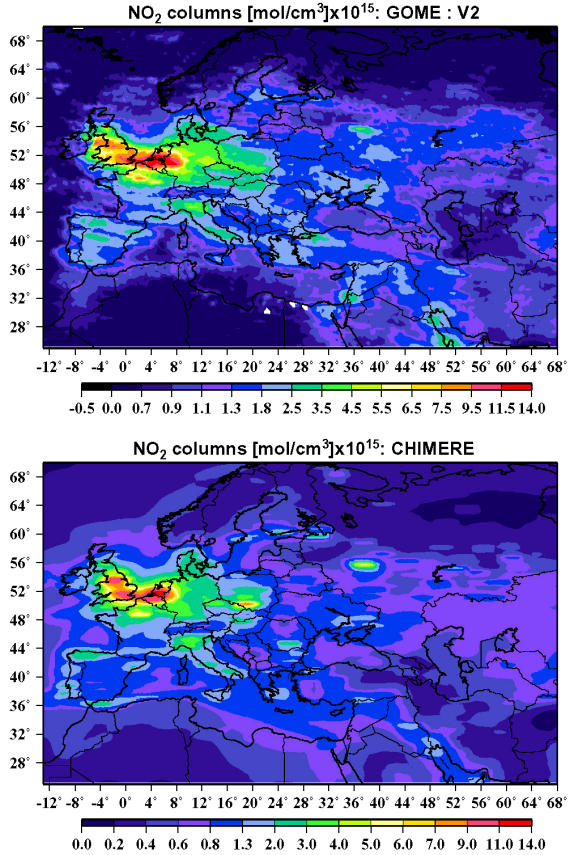

Fig. 4. Distributions of tropospheric NO_2 columns derived from GOME measurements in comparison with lower tropospheric NO_2 columns (above 500 hPa pressure level) simulated with CHIMERE, upper tropospheric NO_2 columns evaluated with MOZART, and composed (CHIMERE plus MOZART) total tropospheric NO_2 columns. The GOME and CHIMERE data represent the averages over the summer months of 1997. Upper tropospheric NO_2 were evaluated by averaging monthly NO_2 MOZART data corresponding to the summer of 1996. Note differences in scales of the plots.

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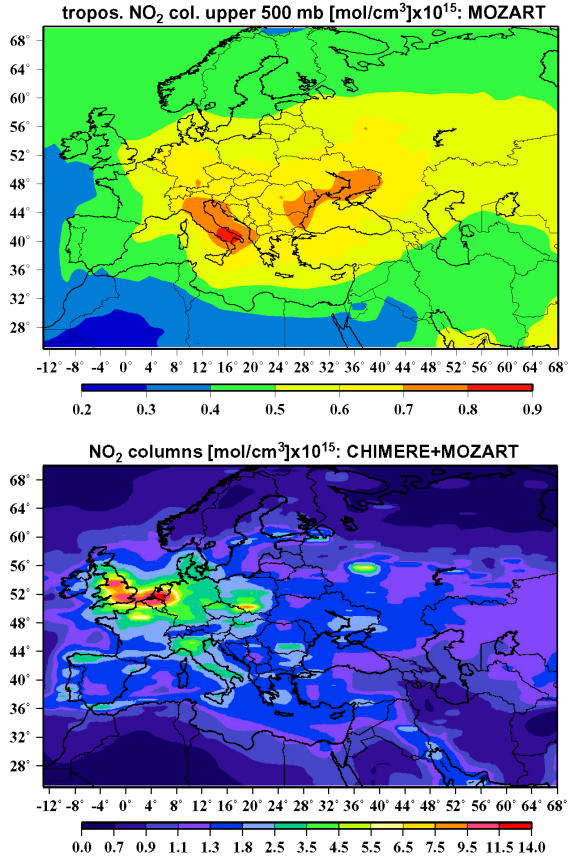

Fig. 4. Continued.

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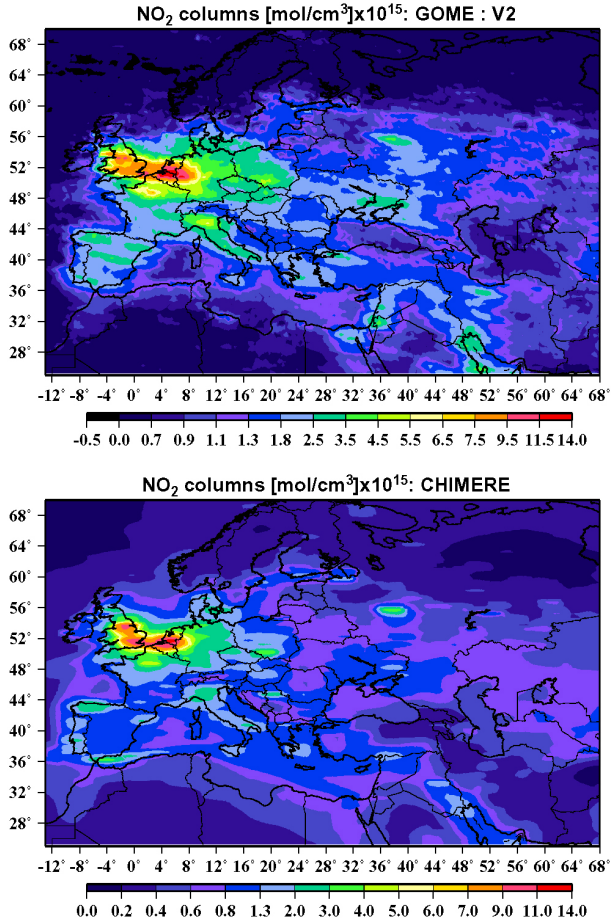

Fig. 5. Distributions of the tropospheric NO_2 columns derived from GOME measurements in comparison with the lower tropospheric NO_2 columns simulated by CHIMERE. The data shown represent the averages over summer months of 2001.

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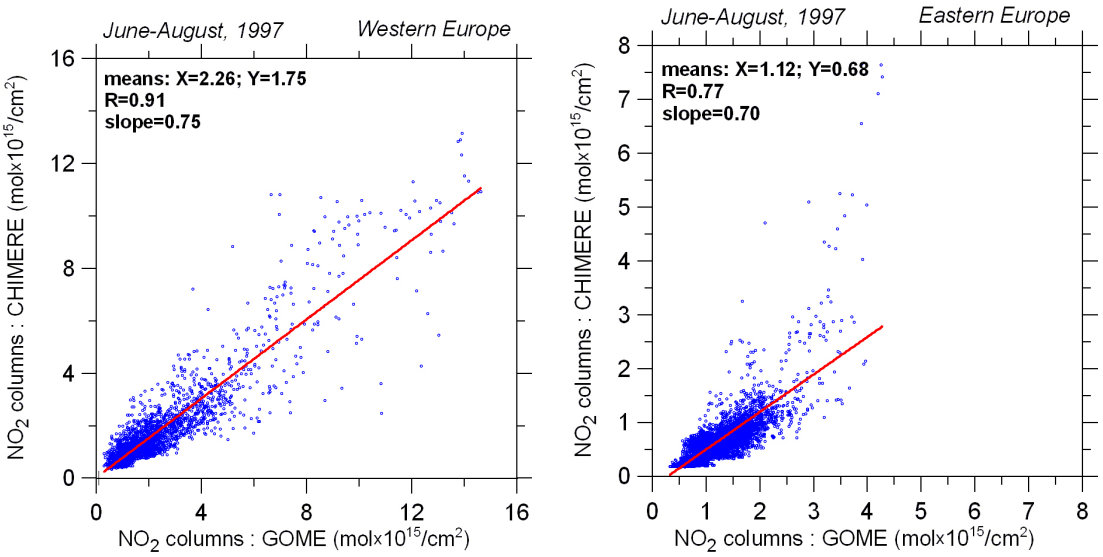

Fig. 6. Scatter plots of the simulated and GOME derived NO_2 columns for Western and Eastern Europe.

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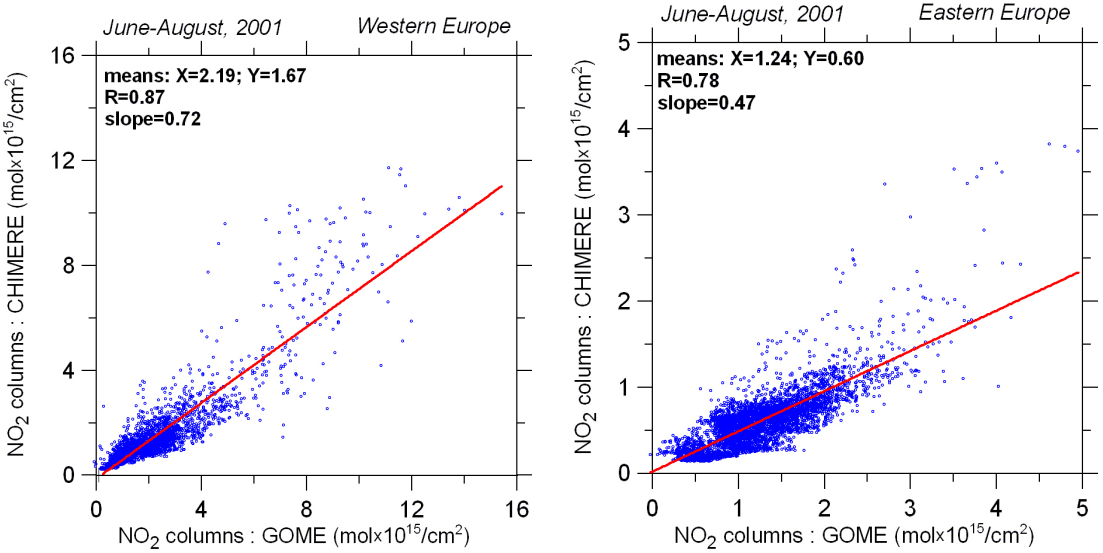

Fig. 6. Continued.

ACPD
4, 6503–6558, 2004

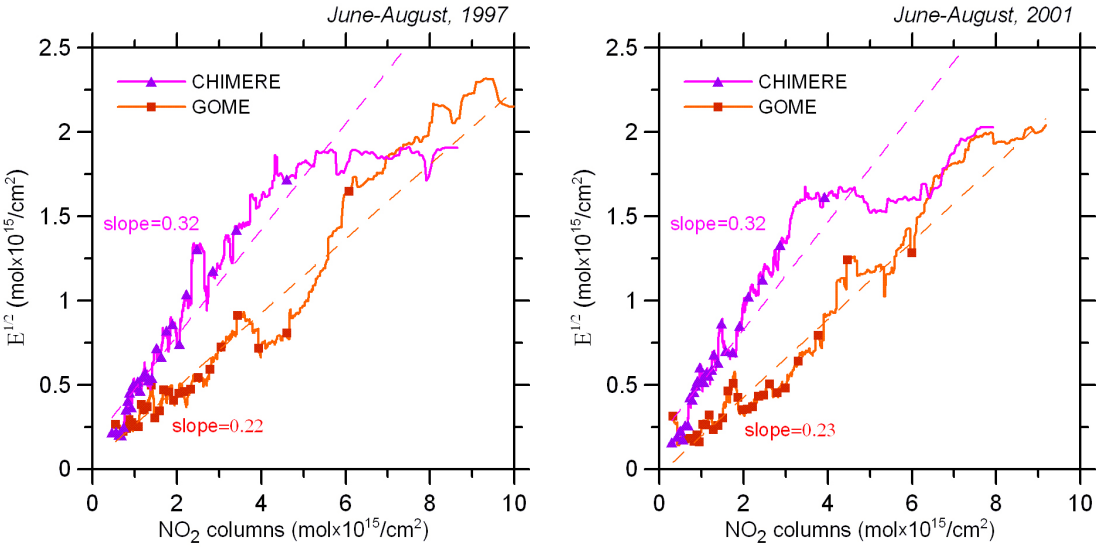

Fig. 7. Running averages of squared differences between the deviations of the simulated and GOME measurement derived tropospheric NO_2 columns from their running mean values versus the running averages of the indicated data for Western Europe. The averaging procedure using a running window covering 100 data points is applied to the gridded data for the seasonally averaged tropospheric NO_2 columns arranged with growing amplitude. The points on the curves are depicted with a frequency of 1/100.

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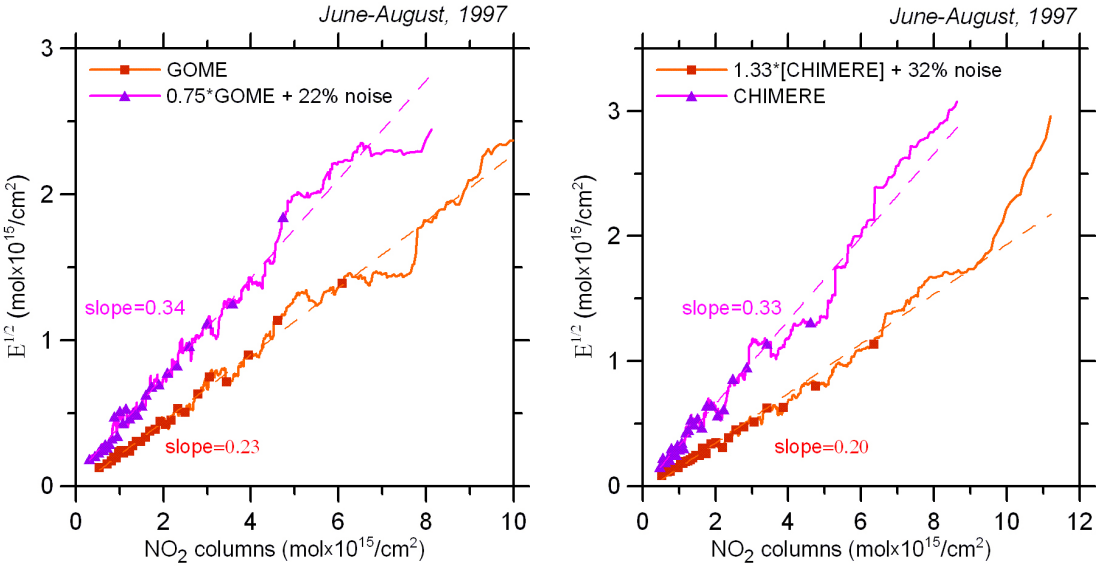

Fig. 8. The interpretation of the results presented in Fig. 7. The plots show the results of the same error analysis as in Fig. 7, but aimed at retrieving the known "errors" of the artificially transformed dataset.

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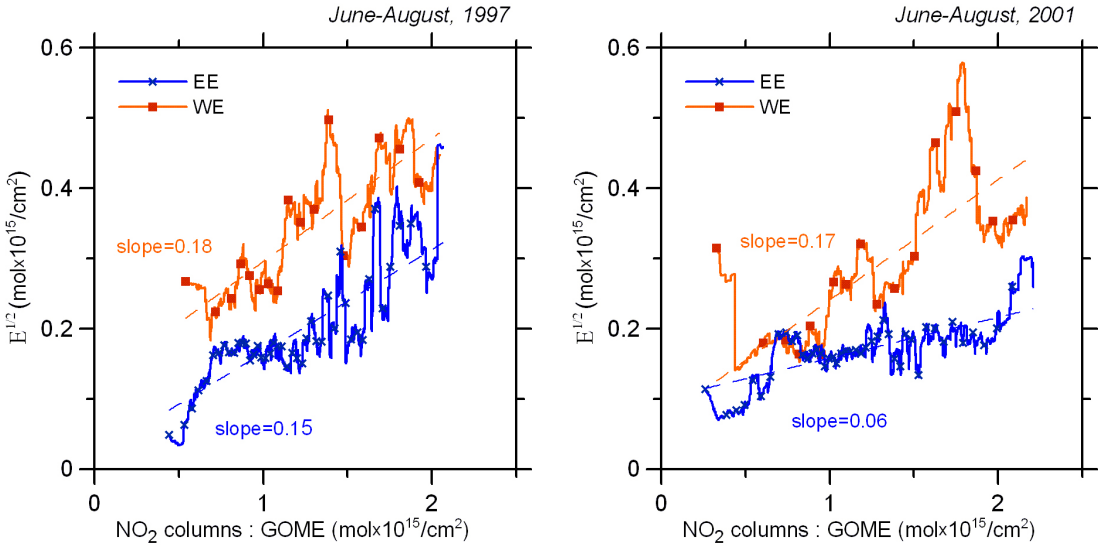

Fig. 9. The same as in Fig. 7, but for Eastern Europe. For convenience, the plots reproduce also fragments of the dependences for Western Europe.

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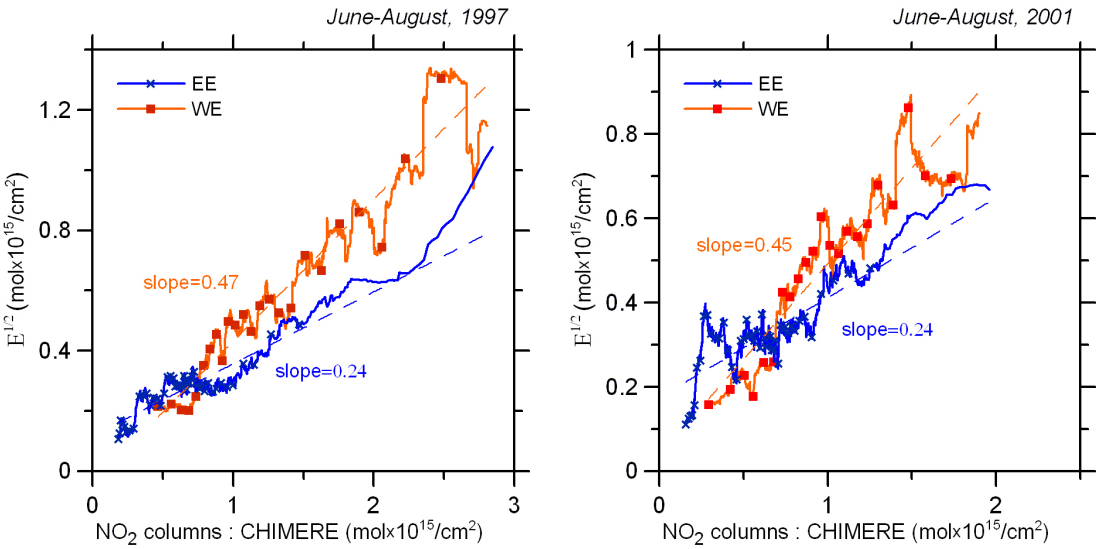

Fig. 9. Continued.

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