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Weekly cycle of NO_2 by GOME measurements: A signature of anthropogenic sources

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Abstract

Nitrogen oxides ($NO+NO_2=NO_x$) are important trace gases in the troposphere with impact on human health, atmospheric chemistry and climate. Besides natural sources (lightning, soil emissions) and biomass burning, fossil fuel combustion is estimated to be responsible for about 50% of the total production of NO_x. Since human activity in industrialized countries largely follows an artificial seven-day cycle, fossil fuel combustion is expected to be reduced during weekends. This "weekend effect" is well known from local, ground based measurements, but has never been analysed on a global scale before.

The Global Ozone Monitoring Experiment (GOME) on board the ESA-satellite ERS-2 allows measurements of NO_2 column densities. Applying sophisticated algorithms, vertical column densities (VCD) of tropospheric NO_2 can be determined. We demonstrate the statistical analysis of weekly cycles of tropospheric NO_2 VCDs for different regions of the world. In the cycles of the industrialized regions and cities in the US, Europe and Japan a clear Sunday minimum of tropospheric NO_2 VCD can be seen. Sunday NO_2 VCDs are about 25–50% lower than working day levels. Metropolitan areas with other religious and cultural backgrounds (Jerusalem, Mecca) show different weekly patterns corresponding to different days of rest. In China, no weekly pattern can be found.

The presence of a weekly cycle in the measured tropospheric NO_2 VCD allows the identification of anthropogenic sources. In addition, the fraction of emissions subjected to a weekly cycle (mainly transport, power generation) with respect to a constant background (all kind of natural sources, biomass burning, heavy industry) can be estimated. Furthermore, we estimated the lifetime of tropospheric NO_2 by analysing the mean weekly cycle over Germany in detail, obtaining a value of about 12 h.

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1. Introduction

Over the last 150 years, the atmospheric composition has changed dramatically due to the industrial revolution. Among the various emitted pollutants nitrogen oxides ($NO+NO_2=NO_x$) play an important role. In the troposphere they have a large impact on human health, climate and atmospheric chemistry, e.g. due to the role they play in ozone production (Atkinson, 2000) and their influence on the OH concentration ("oxidizing power", Jacob, 2003). The estimation of the strengths of the different NO_x sources (industry, biomass burning, aircraft, soil emissions, lightning) still has high uncertainties (Lee et al., 1997). Nevertheless, NO_x by fossil fuel combustion is estimated to account for more than 50% of the overall production.

Industrial activity and traffic in western countries are reduced during weekends leading to lower levels of emitted pollutants ("Weekend effect"; Cleveland et al., 1974; Elkus and Wilson, 1977; Cerveny and Coakley, 2002). Compared to working day levels the weekend emissions of NO_x, e.g. in Germany, are reduced by approximately 35% (Wickert, 2001). The degree of reduction of industrial activity and traffic may differ from country to country and even from region to region, but a Sunday minimum of NO_x emissions is expected at least for countries with a Christian tradition, celebrating Sunday as the day of rest.

Satellite measurements allow a new and independent approach to the determination of trace gas emissions. The entire globe is monitored with a single instrument under the same conditions and over long periods of time. The Global Ozone Monitoring Experiment GOME on board the ESA satellite ERS-2 provides data to determine vertical column densities (VCDs) of NO_2 (Wagner, 1999; Leue et al., 2001). By subtracting the estimated stratospheric fraction, tropospheric VCDs of NO_2 are retrieved (Leue et al., 2001; Velders et al., 2001; Wenig et al., 2001). Since the lifetime of tropospheric NO_2 is of the order of one day (Leue et al., 2001), enhanced VCDs directly indicate nearby sources of NO_x.

Remote sensing of the troposphere in principle is constrained by clouds (Velders et

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al., 2001). Furthermore, the spatial resolution of one GOME ground pixel ($320\times40\,km^2$) is rather coarse compared to the extent of individual cities. In spite of these uncertainties of individual VCD measurements, the statistical analysis of long time series of GOME data provides reliable information, for instance on the mean tropospheric NO_2 distribution and features of its weekly cycle.

2. Retrieval of tropospheric NO_2 vertical column densities from GOME

In April 1995, the ERS-2 satellite was launched by the European Space Agency, carrying (in addition to other instruments) the Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999). The satellite operates at an altitude of about 780 km. It flies along a sun- synchronous polar orbit and crosses the equator at 10:30 (local time). GOME consists of four spectrometers measuring the radiation reflected by the earth in the UV/vis spectral range with a resolution of about 0.2–0.4 nm. Global coverage is achieved every three days. The primary objective of GOME is the retrieval of Ozone column densities, but beyond this the column densities of several trace gases can be determined by applying Differential Optical Absorption Spectroscopy (DOAS) (Platt, 1994). The retrieval of vertical column densities (VCDs) of NO_2 is described in detail by Wagner (1999), Leue et al. (2001) and Wenig (2001).

Since the global distribution of stratospheric NO_2 is much more homogeneous and less time dependent than it is in the troposphere, it is possible to estimate the stratospheric fraction of the total column (Leue et al., 2001; Velders et al., 2001; Wenig, 2001). For this study, the stratospheric column was determined in a reference sector over the remote Pacific (Richter and Burrows, 2002). The difference between the total and the stratospheric column represents the tropospheric fraction. For a quantitative analysis the tropospheric vertical column density has to be corrected for effects of radiation transport in the troposphere. The absolute value of the correction factor depends on surface albedo, trace gas profile and especially the cloud cover (Richter and Burrows, 2002; Martin et al., 2002). In this study, we apply a uniform correction factor of

4 (Velders et al., 2001) to keep the analysis as simple as possible. We focus on the relations of mean VCDs of different days of the week, i.e. normalized weekly cycles, which should be independent of the correction factor.

The coverage of one GOME pixel is about 40 km north-south by 320 km east-west. This complicates the monitoring of individual cities: the total area of pixels containing a specific location is $80 \times 640\,km^2$ (since the city center may be situated in the upper right corner of the GOME pixel as well as in the lower left corner), implying possible interferences with other sources.

The flight track of the ERS-2 satellite has a periodicity of 35 days. That means, that every 35 days the GOME ground pixel coordinates are identical. This circumstance may influence the analysis of weekly cycles, since 35 is a multiple of 7. Hence each day of the week is scanned with a different spatial sampling. This implies that, by monitoring a certain location, the influence of neighbouring regions differs from day to day. This effect is in general of minor importance, but may cause artefacts in the weekly cycle of tropospheric NO_2 VCD in a few cases (see below).

The retrieval of tropospheric information from satellite data can be strongly affected by clouds: an enhanced cloud cover might "shield" the troposphere and lead to a reduced observed VCD. In principle, there could even be a systematic weekly cycle of cloud cover. In fact, Cerveny and Balling Jr (1998) report a weekly cycle of precipitation. To check a possible weekly cycle of cloud cover we use the Heidelberg Iterative Cloud Retrieval Utilities (HICRU), recently presented by Grzegorski (2003). HICRU contains an improved algorithm that retrieves cloud covers using the GOME Polarization Monitoring Devices (PMD), which are broad band spectrometers with a better spatial resolution. Therefore, cloud cover information at the same time and place as for the NO_2 retrieval is obtained.

By analysing the weekly cycle of the HICRU cloud cover data we found no indication for a weekly pattern of enhanced cloud cover on Sundays. In the case of Germany, for instance, the cloud cover ranges from 43% (Tuesday) to 48% (Friday) with a Sunday value of 46% (mean of 1996–2001).

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The GOME measurements currently span more than 7 years, providing a large amount of data for statistical evaluation. Figure 1 shows the mean global distribution of tropospheric NO_2 VCDs for 1996–2001. Regions with high industrial activity and even individual metropolises, e.g. Mexico City, can clearly be seen. In this study, we focus on four regions of the world with enhanced NO_2 VCD values: 1. the eastern USA, 2. western Central Europe, 3. East Asia and 4. the Middle East, as well as 5. some individual cities, as marked in Fig. 1.

3. Weekly cycle of tropospheric NO_2 VCD

The weekly cycle of tropospheric NO_2 VCD is visualized in two ways. Figure 2 shows maps of the tropospheric NO_2 VCD for the regions under consideration for the different days of the week (mean over 1996–2001). This provides information about the absolute source strength in the different regions. The effect of the 35 day periodicity of GOME is reflected by the stripe-like structures parallel to the ERS-2 flight direction.

In addition, Fig. 3 shows plots of weekly cycles for some selected cities. The values are normalized to the median weekly value for better comparison. The focus of this plot is the relative reduction of the tropospheric NO_2 VCD during the day of rest.

Both figures show the same general features: the level of NO_2 VCD is similar for the different working days, but there is a significant reduction of tropospheric NO_2 VCD during the weekend, especially on Sunday, for the US (1), Europe (2), and Japan (3a). In all cities considered in these regions, there is a minimum on Sunday. The NO_2 VCD is reduced by about 25–50% and even 60% (Milan (2)). A Sunday minimum can also be seen in Johannesburg and Mexico City (5).

In China (3b), no indications for a weekly cycle can be found in Figs. 2 or 3. China has a different economic, cultural, and religious background. Nevertheless, there also is a seven day week and a work free weekend. The absence of a weekend effect in our data probably indicates that the Chinese NO_x emissions are dominated by power plants and heavy industry, operating throughout the week. On the other hand, in the

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US and in Europe individual transport appears to contribute significantly to the NO_x sources.

The cities in the Middle East (4) show a shifted weekly cycle due to different religious traditions, i.e. other days of rest. In Israel, Saturday (Sabbath) is the day of lowest NO_2 VCD. In Islamic cities, there is a slight weekly effect with lowest emissions on Friday.

Besides the noticeable minimum on Sunday, there are two more days of interest in the weekly cycles of the western cities: a) Saturday, since it is also a working free day for most professions in western countries (reduced industrial activity), but a preferred day for shopping or short trips (possible increase of individual transport), and b) Monday, since it starts with relatively clean air, whereas for the other working days the measured air masses might be influenced by the pollution of the day before, as the lifetime of NO_2 in the troposphere is about one day.

a) Saturday NO_2 values are slightly reduced in most western cities. But in some places they are quite high, reaching normal working day levels (e.g. Milan, Dallas, Tokyo).

b) Monday values in the US and Europe are almost on working day level, whereas there are uncommonly low levels in Tokyo and Seoul (3a) as well as in Sao Paulo and Jakarta (5).

To understand these features in the weekly cycle in detail, further information about local emissions, wind force and direction, and lifetime of NO_2 is necessary. Another aspect is the daily cycle of emissions, especially the starting time of work in the morning which differs from region to region, whereas the local observation time of GOME is the same.

The 35 day periodicity of the ERS-2 satellite flight track should be, in general, of minor influence. However, it is thought to be the most probable reason for some unusually high values, e.g. the Tuesday values in Essen or the high Wednesday values in Sheffield (Fig. 3(2)). For instance, in the Tuesday scans, the polluted regions of West Germany (Ruhr area) and the Netherlands are largely covered by a single track of GOME pixels, whereas there are two neighbouring tracks on Wednesdays (see Fig. 2(2)). This leads to a higher observed NO_2 VCD on Tuesdays compared to

Wednesdays.

The presence of a weekly cycle underlines the significance of estimates of tropospheric NO_2 VCD. The existence of a weekly cycle can serve as an indicator (but not necessarily, see China) for anthropogenic sources.

4. Lifetime estimation

Since the tropospheric lifetime of NO_2 is of the order of one day, the low Sunday emissions should have an influence on the VCD measured on Monday in the area downwind from the source regions. This is analysed in detail for Germany, i.e. the area 7°–14° E and 48°–54° N (Fig. 4). Since the main source regions are located in the western part of Germany and the mean wind direction is eastwards, the emitted pollutants remain within the area for at least one day. (A mean wind velocity of approx. 5 m/s corresponds to a daily transport of 432 km, whereas the east-west extension of Germany is about 700 km.)

Therefore the lifetime of NO_2 in the troposphere can be roughly estimated. We have based our analysis on some simple assumptions:

1. There is a constant NO_x emission during daytime (12 h), while there are no emissions at night. Saturday emissions are 66%, Sunday emissions 60% of working day level (adopted from Wickert, 2001), see Fig. 5a.

2. The loss of NO_2 due to photochemical processes is assumed to be an exponential drop with a constant lifetime τ.

3. There is no loss due to wind transport of NO_2 out of the considered area.

Therefore, the change of the NO_2 VCD can be described as

$$d(VCD_{NO_2})/dt = E(t) - (VCD_{NO_2})/\tau$$

E(t): Emissions (in units of molecules $cm^{-2} s^{-1}$).

This differential equation was solved numerically. Figure 5b shows the retrieved mean German NO_2 VCD at the ERS-2 overpass time for different lifetimes τ. This is compared to the actual measurements of GOME in Fig. 5c.

The Sunday reduction is underestimated in the modelled weekly cycle. This might indicate that the reduction of weekend emissions is actually more extensive than assumed. In any case, the detailed temporal pattern of the weekly cycle of the modelled VCD crucially depends on the assumed lifetime. A lifetime of 6 h and shorter leads to a weekly cycle similar to that of the emissions, i.e. the Saturday values are almost as low as Sunday values and Monday values are similar to those of the other workdays. On the other hand, a lifetime of 18 h leads to Monday values much lower than Saturday values, which could not be observed (see Fig. 5).

For this study, a lifetime of tropospheric NO_2 of about 12 h fits best. This may be different for other regions and has different effects on the weekly cycle, i.e. the Saturday and Monday values.

5. Conclusions

The existence of a weekly cycle is an obvious signature of anthropogenic sources. In most western industrialised areas a clear weekly cycle with a noticeable Sunday minimum can be found in tropospheric NO_2 VCD from GOME, underlining the power of tropospheric trace gas measurements from space. Regions with a different religious background show a shifted weekly cycle with minimum NO_2 VCD on Saturday (Israel) or Friday (Islamic cities). In China, no weekly cycle of tropospheric NO_2 could be found.

The low level of the Sunday minimum in the western cities provides information about the fraction of periodic anthropogenic sources of NO_x. This helps to discriminate man-made from natural sources (lightning, biomass burning, soil emissions) and assess the contribution of local traffic to the NO_x sources.

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Furthermore, the characteristics of the weekly cycle, i.e. the ratio of the Monday values and Sunday minima, allow to deduce the lifetime of tropospheric NO_2.

The usability of these methods requires background information about the considered regions. Weekly patterns of emissions, the predominant source of NO_x (traffic, heavy industry or heating) and the lifetime of tropospheric NO_2 differ for different levels of industrialisation, religious and cultural customs and meteorological conditions. Further information can be gathered by analysing the weekly cycle of summer and winter data separately, since the role of traffic compared to heating should be different for both cases.

The statistical errors of the data points in Fig. 3 are quite small due to the large amount of data. Systematical errors due to the large spatial extent of the GOME pixels, as described in Sect. 2, have to be borne in mind. A better spatial resolution (nominal $30 \times 60\,km^2$) will be provided by the SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) onboard the ENVISAT, which is presently in its validation phase. Furthermore, due to the additional limb viewing geometry a direct estimation of the stratospheric column is possible. Time series of SCIAMACHY data as well as ongoing GOME measurements will allow the improved analysis of weekly cycles of tropospheric NO_2 and will afford quantitative estimates of different types of anthropogenic emissions as well as the lifetime of tropospheric NO_2 for different regions of the world.

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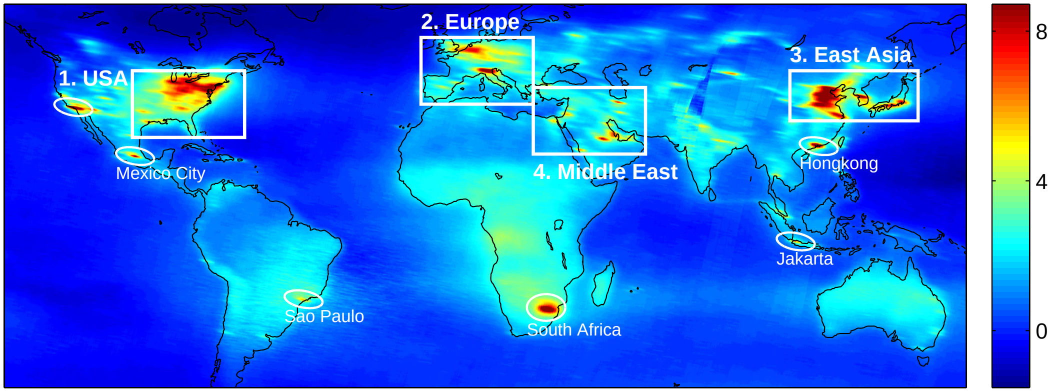

Fig. 1. Six years mean (1996–2001) of global tropospheric NO_2 Vertical Column Density in 10^{15} molecules/cm^2. The weekly cycle of the framed areas 1. US East Coast, 2. Europe, 3. East Asia and 4. Middle East, as well as 5. the marked individual metropolises are considered in detail in this study.

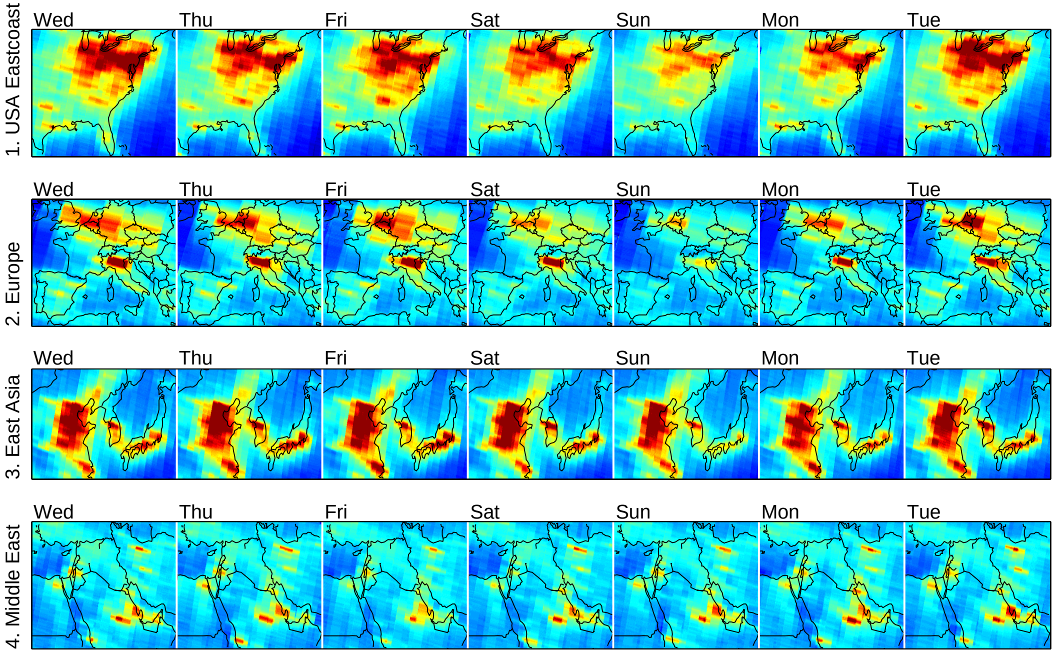

Fig. 2. Mean tropospheric NO_2 VCD (1996–2001) for the regions of interest, as marked in Fig. 1, for the different days of the week separately. Colour scale and unit are the same as in Fig. 1.

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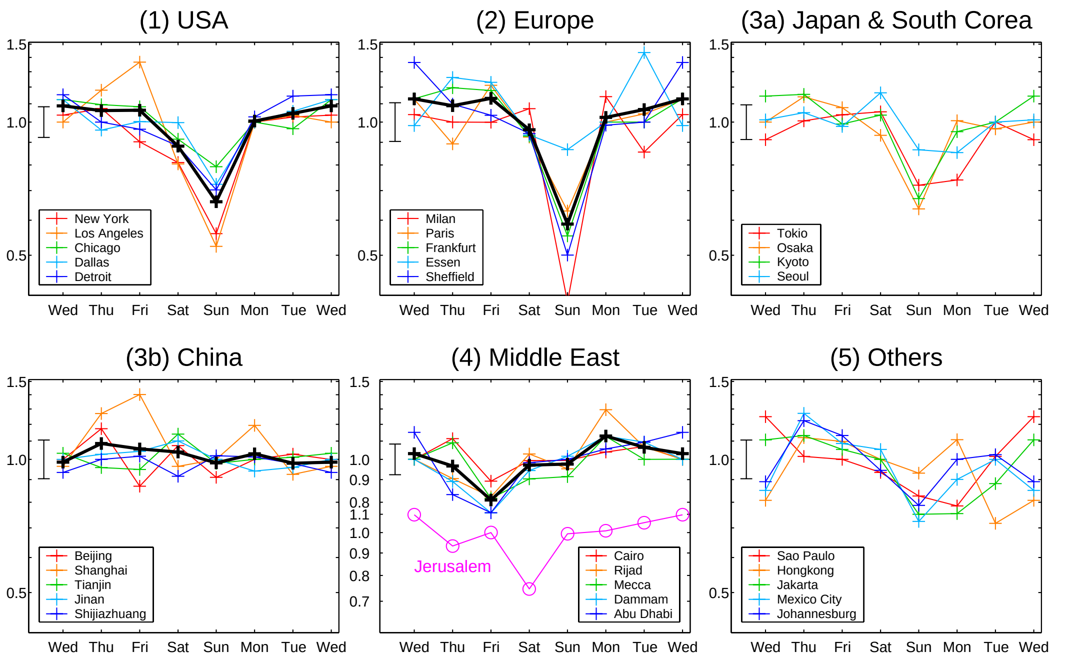

Fig. 3. Weekly cycle of tropospheric NO_2 VCD for the considered locations (as marked in Fig. 1). The values are normalized with respect to the median weekly value (relative units). Black lines are averaged curves. The error bar to the left of every plot indicates the maximum error (standard error of the mean) of all data points.

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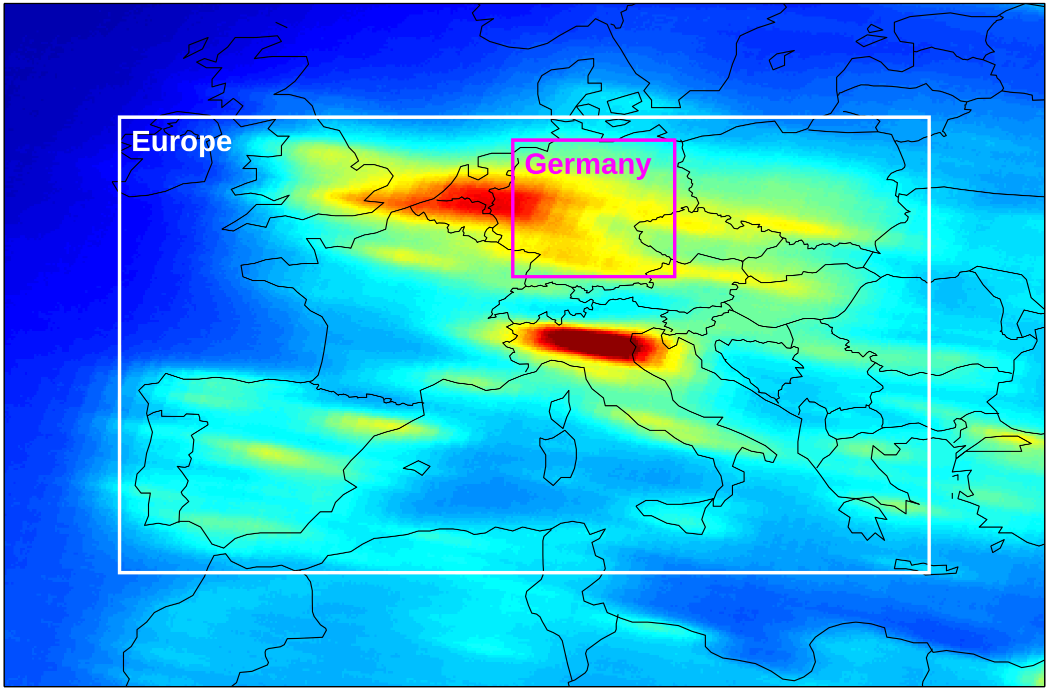

Fig. 4. Zoom of Fig. 1 on West Europe. For the lifetime estimation of tropospheric NO_2 in Germany, the considered area is marked (7°–14° E and 48°–54° N).

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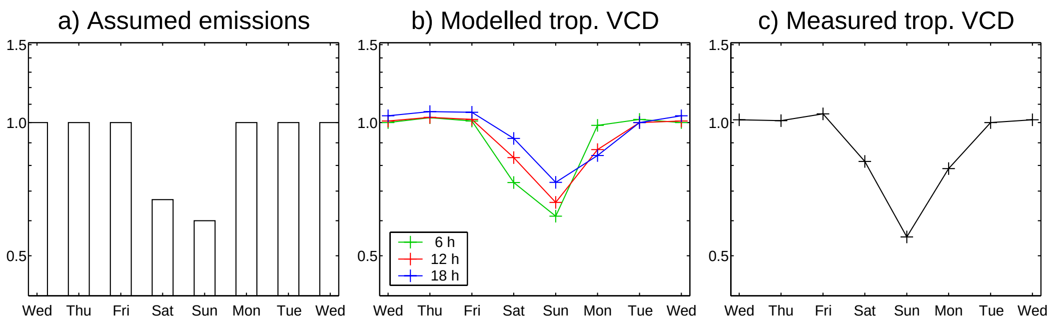

Fig. 5. Weekly cycle of NO_2 (modelled and measured) for Germany (as shown in Fig. 4). All plots are normalized with respect to the median weekly value (relative units). **(a)** Assumed weekly cycle of NO_x emissions (Adopted from Wickert, 2001). **(b)** Modelled tropospheric VCD at ERS-2 overflight time for different lifetimes of NO_2. **(c)** Mean tropospheric VCD of NO_2 measured with GOME.