**Atmospheric
Chemistry
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Discussions**

A modelling study of photochemical regimes over Europe: robustness and variability

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Abstract

The variability of the relative sensitivity to volatile organic compounds (VOC) or NO_x emissions, the chemical regime, over Europe during summers 2001 to 2003 is simulated with a regional scale transport-chemistry model. The robustness of chemi-
cal regimes is shown. A VOC sensitive regime over North-Western Europe and a mainly NO_x sensitive regime over the Mediterranean basin and Eastern Europe are found, confirming earlier published results. The chemical regime time variability, its robustness to several environmental factors (seasonality, interannual variability) and to model uncertainty are thoroughly analysed. The chemical regime spatial struc-
ture only slightly depends on the ozone target considered (daily ozone maximum or AOT40, SOMO35, ...). Differences between particular years and summer months are weak. Day to day variability is significant but does not change the occurrence of one or another chemical regime over North-Western Europe and the Mediterranean basin. Expected decreases in anthropogenic NO_x emissions over Europe since the last and
for the next few decades have shifted and will shift chemical regimes to more NO_x sensitive. The predictive and explanatory use of chemical regime indicator species is also investigated. For all cases but near ship tracks over the Mediterranean basin, the spatial pattern of chemical regimes appears to be robust with respect to model uncertainty.

1 Introduction

The relation between pollutant emissions and concentrations of gases and aerosols affecting health and ecosystems is nonlinear. That is why the management of air quality requires adequate emission control strategies. Photo-oxidant pollution, due to ozone and related trace gases, has a complex sensitivity to primary precursor emission families. The exact knowledge of this sensitivity is necessary for the management of this type of atmospheric pollution. A particular attention has been given to the question

whether either nitrogen oxides (NO_x) or volatile organic carbon species (VOC) emission reductions are more suitable to limit ozone pollution (e.g. Sillman et al., 1999; Milford, 1994). Chemical regimes have been defined relating ozone concentrations to upwind precursor emissions: in the "NO_x sensitive chemical regime", NO_x anthropogenic
5 emission reductions are more efficient to reduce ozone levels than VOC anthropogenic emission reductions (Sillman et al., 1995), and the reverse occurs in the "VOC sensitive chemical regime". Alternatively, Kleinman et al. (1997) defined chemical regimes in terms of sensitivity of *local photochemical ozone production* (PO_3) with respect to NO_x and VOC concentrations (instead of emissions). They showed theoretically that
10 a locally VOC sensitive chemical regime is related to a dominant odd hydrogen (HO_x) radical loss through reactions between NO_x and HO_x species, whereas a NO_x sensitive chemical regime is related to dominant loss through HO_x recombination reactions. This framework allows explaining the spatial and temporal variability of photochemical regimes with respect to environmental conditions: Large NO_x emissions and concen-
15 trations favour a VOC sensitive chemical regime, large VOC emissions and concentrations, and large HO_x production rates favour a NO_x sensitive chemical regime. For a given VOC/NO_x concentration ratio, larger concentrations favour a VOC sensitive chemical regime.

Many modelling-based or observation-based studies have addressed the spatial and
20 temporal variability of chemical regimes at urban locations and on regional scale. Using models the chemical regimes can be determined using twin simulation experiments, while from observations trace gas ratios indicating the nature of the chemical regime are used (e.g., Sillman, 1995).

Due to large emissions and low VOC/NO_x concentration ratios (as compared to rural
25 background), chemical regimes during ozone pollution episodes have been shown to be generally VOC sensitive for large urban agglomerations: this has been made evident for large North American agglomerations (Los Angeles, Sillman et al., 1997; New York, Philadelphia, Phoenix, Kleinman et al., 2005; Mexico City, Lei et al., 2007), for North-Eastern Asian Megacities during spring (Beijing, Seoul, Tokyo, Guttikunda et al.,

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2005) and for many European agglomerations as Milano (Spirig et al., 2002; Martilli et al., 2002; Gabusi et al., 2005), Athens (Bossioli et al., 2007), Berlin (Hammer et al., 2002) and Paris (Beekmann et al., 2003; Deguillaume et al., 2008). However, for many of these cases, transitions to NO_x sensitive chemical regimes occur in the plume of these agglomerations at variable distances. NO_x sensitive or neutral (near transition NO_x-VOC sensitivity) chemical regimes agglomerations can also occur within agglomerations with enhanced VOC/NO_x ratios due to large biogenic (Atlanta, Sillman et al., 1995; Nashville, Kleinman et al., 2005) or anthropogenic VOC sources for example due to refineries (Houston, Kleinman et al., 2005; Fos-Berre sector in southern France, Coll et al., 2005; and Paris in some circumstances, Sillman et al., 2003). To some extent, simulated chemical regimes can also depend on the model resolution as shown for several European agglomerations (Thunis et al., 2007). For simulations with an urban scale resolution (5 km), the VOC sensitive chemical regime for Milano and Prague is more pronounced than for models with a regional scale resolution (50 km), but differences were also large between different models of same resolution.

Contrary to urban areas, rural areas are generally NO_x sensitive during summer. This conclusion was obtained from simulations for US using several chemistry-transport models (Liang et al., 1998; Pierce et al., 1998), the latter study pointing to the large influence of biogenic VOC emissions to maintain the NO_x sensitive regime even over more polluted areas of north-eastern US. Simulations with the EMEP unified Eulerian model show a NO_x sensitive regime over the Mediterranean region, but a VOC sensitive regime over polluted parts of North-Western Europe (Tarrason et al., 2003), the latter being confirmed by a study of Derwent et al. (2003). Over Germany, results are ambiguous: a NO_x sensitive chemical regime has been simulated with the EMEP unified Eulerian model for summer 2000 with respect to accumulated ozone over the 60 ppb threshold (AOT60). On the contrary, a VOC sensitive regime has been simulated with the lagrangian EMEP trajectory model for 1990 emissions with respect to AOT60 (Simpson et al., 1997). A chemical regime tracer method based on tropospheric HCHO to NO_2 columns indicates a VOC sensitive regime over parts of Western

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Germany and a NO_x sensitive regime elsewhere (Martin et al., 2004).

From the previous overview, it appears that uncertainties in chemical regime calculations over Europe are still large, and that a comprehensive study addressing both its spatial and temporal variability is still missing. Thus, in this work, we propose a systematic study of chemical regimes over Europe using a state of the art continental scale chemistry-transport model (CHIMERE). In addition to previous studies, we first evaluate how robust the simulated chemical regimes are with respect to the ozone target chosen, with respect to the time period of the simulation (year, month, day), and with respect to model uncertainties. Second, we also link chemical regimes variability to simulated trace gas ratios, which can be used as explanatory tool to assess the influence of emissions or meteorology on the regimes. The study aims at making evident regional scale features which are still resolved in a continental scale simulation with a 0.5° horizontal resolution. Thus finer scale urban features can not be addressed in this study.

The paper is organised as follows. In Sect. 2, the set-up of the chemistry-transport model is described; the study design is explained. Results are given in Sect. 3 presenting first the spatial structure of the time averaged chemical regime and its dependency on the ozone target (Sect. 3.1) and its relation to chemical regime tracer species (Sect. 3.2). Its time variability on decadal to daily scales is analysed in Sects. 3.3 and 3.4. The robustness of the chemical regimes with respect to model uncertainty is discussed in Sect. 4. Conclusions are given in Sect. 5.

2 Methods

2.1 CHIMERE chemistry-transport model

The model used in this study is the eulerian regional chemistry-transport model named CHIMERE (Schmidt et al., 2001) (see http://www.lmd.polytechnique.fr/chimere/). The model has been applied to simulate and analyse pollution episodes at regional (Vautard

et al., 2005; Hodzic et al., 2006) and urban scale (Vautard et al., 2003; Coll et al., 2005), to analyse the sensitivity to anthropogenic (Menut et al., 2003) and biogenic emissions (Derognat et al., 2003; Curci et al., 2008) for long-term ozone trends analysis (Vautard et al., 2006), and for diagnostics or inverse modelling of emissions (Vautard et al.,
5   2003; Deguillaume et al., 2007; Konovalov et al., 2006, 2008; Pison et al., 2007). The model has also been used for several years for operational forecast of pollutant levels over Western Europe (Honoré et al., 2008; http://www.prevair.org).

The model uses a $0.5° \times 0.5°$ horizontal grid covering all Europe ([35°–57° N; 10° W– 22° E]), with 8 hybrid-sigma vertical layers extending to 500 hPa. Meteorological input
10   is provided by PSU/NCAR MM5 model (Dudhia, 1993) simulations on a Mercator grid with an approximate $30 km \times 30 km$ (at 50° N) horizontal resolution and 32 vertical sigma layers extending up to 100 hPa. The model is forced by the ECMWF ERA-40 reanal- ysis (before 1 September 2002) or operational ECMWF analyses (afterwards) taken at $1.125° \times 1.125°$ and using the grid nudging (grid FDDA) option implemented within
15   MM5. MM5 simulations are actually carried out by pieces of 5 days and 6 h, starting at 18:00 UT and removing the first 6 h (spin-up period) for the CHIMERE forcing.

Anthropogenic emission data used are based on the so-called "expert" annual data of the EMEP emission inventory (Vestreng et al., 2005) for the year 2002. Annual totals are disaggregated using monthly, daily and hourly factors (Friedrich, 1997) and
20   a speciation of non-methane volatile organic compounds (NMVOC) (Passant et al., 2002). VOC emissions are aggregated into 11 model classes following the mass and reactivity weighting procedure proposed by Middleton et al. (1990). Biogenic emissions for isoprene, terpenes and NO are implemented following the methodology described in Simpson et al. (1999).
25   CHIMERE uses the MELCHIOR gas-phase chemical mechanism (Lattuati, 1997). From the complete mechanism ($\sim$80 compounds, 320 reactions), a reduced mecha- nism has been derived (Derognat, 2002) according to the concept of chemical oper- ators (Aumont et al., 1996): it includes 44 chemical species and about 120 reactions and is used for this study, but a sensitivity experiment is performed with the extended

mechanism.

Chemical boundary conditions for long-lived species are provided by a monthly mean global climatology from LMDz-INCA model (Hauglustaine et al., 2004). The numerical method for the temporal solution of the stiff system of partial differential equations is adapted from the second-order TWOSTEP algorithm originally proposed by Verwer (1994).

The CHIMERE model has been extensively compared to observations. The most complete comparison has been performed in the frame of the evaluation of the PREVAIR system, in which CHIMERE is used for continental scale pollution forecast, for a period covering three spring/summers seasons (April to September) in 2004 to 2006 (Honoré et al., 2008). For 149 rural and 84 suburban sites in Western and Central Europe, the average bias in daily maximum surface ozone was respectively 1.7 and 3.6 μg/m^3. The range in bias for individual sites is in general between $\pm$15 μg/m^3. The model has a tendency to overestimate daily ozone maxima over maritime areas and coastal areas and underestimates them over continental, central areas. RMSE (root mean square error) was 16.8 and 17.6 μg/m^3 and correlation was 0.83 for both types of sites. The model catches 35% of 180 μg/m^3 exceedances, and gives very little false alarms, thus high ozone values tend to be underestimated (a feature which can be partly corrected by statistical adaptation for ozone forecast, Honoré et al., 2008). On the contrary, during the heat-wave in August 2003, high ozone values over Western Europe (in terms of AOT60, i.e. exceedance of the 60 ppb or 120 μg/m^3 threshold) were simulated without significant bias (Vautard et al., 2005). This is important, because during the heat-wave period contributed to a large fraction of high ozone episodes during the study period (see below). The model results for ozone have also been compared with other models at the regional scale (van Loon et al., 2007). Despite a positive ozone bias partly due to other than usual boundary conditions taken in these experiments, the simulated ozone variability reaches a quality lying among the closest to observations.

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2.2 Set-up of the study

The study is performed over three summer periods (May to August). Three different years (2001, 2002 and 2003) are chosen to be able to account for interannual variability in the results. For each summer, a reference simulation and two simulations with either anthropogenic NO_x or NMVOC emissions uniformly reduced by 30% are performed. The chemical regime is then calculated, for each model grid and time step, as the difference in ozone concentrations between the NO_x emission and the VOC emission reduction scenario:

$$D\_O_3 = O_3(E_{NO_x} - 30\%) - O_3(E_{VOC} - 30\%). \tag{1}$$

In this way, a VOC (NO_x) sensitive regime is characterised by positive (negative) values, i.e. as outlined in the Introduction, a VOC (NO_x) sensitive regime corresponds to the case where VOC (NO_x) emission reductions are more efficient to reduce ozone values. The chemical regime is not only calculated for average ozone concentrations, but for a series different ozone targets, defined below, and which have been used as indicators for air quality management. The term "O_3" in Eq. (1) can stand for one of the following ozone targets:

  – Daily ozone average: the most basic term for indicating ozone concentrations;

  – Daily ozone maximum: gives more weight to afternoon photochemical ozone build-up;

  – Daily O_X maximum, with $O_X = O_3 + NO_2$; this term normalises out O_3 titration by NO;

  – AOT40, AOT60 and AOT90 [ppb h]: $\sum_{hours} \max[([O_3] - 40, 60, 90\,ppb), 0]$; Accumulated ozone above respectively a 40, 60 and 90 ppb threshold, integrated over the three summers; AOT40 is used as an indicator for ozone impact on vegetation, AOT60 as an indicator for ozone impact on human health; AOT90 indicates exceedance of the air quality information threshold of $180\,\mu g/m^3$ or 90 ppb.

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- SOMO35 [ppb d]: $\sum_{\text{days}}$ max[(daily maximum 8 hozone mean-35 ppb), 0]; this indicator (Amann et al., 2005) for the ozone health impact corresponds to the accumulation of the highest 8 h ozone mean during each day above a 35 ppb threshold.

Indeed, one of the objectives of the study is to evaluate possible differences in the chemical regimes for these different ozone targets.

3 Results

Here results of the chemical regime calculations for the European domain are presented. First, the average chemical regime over Europe is estimated from simulations over three summer periods. Then, the seasonal and interannual dependence will be addressed. For specific regions, the daily variability will be analysed and compared to modelled chemical regime tracers. Last the long term chemical regime variability will be estimated for past (1980, 1990) and future (2010, 2020) emission scenarios.

3.1 Average chemical regime

The reference simulation (Fig. 1a) over three summer (May to August) periods shows largest average daily surface ozone maxima (O_3^{max}) over the Po valley and neighbouring areas (O_3^{max} above 70 ppb) and over the Mediterranean basin (O_3^{max} above 60 ppb). Ozone values decrease gradually with distance from the Mediterranean basin, down to 40 ppb over the British Islands. The scenario with a uniform 30% decrease in anthropogenic NO_x emissions results in O_3^{max} reductions between 3 and 5 ppb over the Mediterranean basin and over Italy. These are indicated in Fig. 1b as negative values. On the contrary, over North-Western Europe, the NO_x emission reductions cause an O_3^{max} increase, most pronounced over the channel region and the Paris agglomeration (>3 ppb). Also the ship tracks between Spain and North Africa show an increase (>2 ppb). A uniform 30% decrease in anthropogenic VOC emissions results in O_3^{max}

reductions over the whole model domain, especially large (>2 ppb) over big agglomerations like the London area, parts of Benelux, the Rhine Ruhr area, the Paris agglomeration, the Po valley, Genoa, Naples and Barcelona (Fig. 1c). Note that differences between the scenario run and the reference are inverted in Fig. 1c with respect to

5 Fig. 1b, because this allows simply adding Fig. 1b and c in order to obtain the chemical regime (as the difference between the NO_x and the VOC emission reduction scenario, following Eq. 1). Negative values in the south-eastern part of the domain and especially over the Mediterranean basin (<−2 ppb) denote a NO_x sensitive chemical regime (Fig. 1d). On the contrary, strongly positive values over North-Western Europe (up

10 to 7 ppb over the Channel region) indicate a VOC sensitive regime. For this region, both the negative response to NO_x emission and the positive response to VOC emission changes contribute about equally to the resulting regime. The major ship track off the North African coast also shows a VOC sensitive regime. On the contrary, for the Mediterranean basin, NO_x and VOC emission reductions are in concurrence in terms

15 of O_3^{max} reductions, the effect of NO_x emission reductions being larger outside of big agglomerations. Also over most of Germany, both NO_x and VOC emission reductions are efficient and of equal magnitude resulting in a near neutral chemical regime. The major delimitation line in Northern France between a VOC sensitive chemical regime in North-West Europe and a NO_x sensitive regime over Southern and Eastern Europe

20 (Fig. 1d) is already apparent in the NO_x reduction scenario (Fig. 1b).

Next, we investigate how the chemical regime depends on the considered target (always for the average of the three summer periods). For the daily O_x (defined as $O_3 + NO_2$) maximum (Fig. 2a and b), the chemical regime structure is similar to that for O_3^{max}, but values are shifted to less positive over North Western Europe (up to 5 ppb

25 instead of up to 7 ppb for O_3^{max}, Fig. 2b). This results from the ozone titration with fresh NO emissions, which is, together with radical removal through nitric acid formation, the other main ozone build-up inhibition in areas with high NO_x burden.

For daily mean ozone (O_3^{moy}, Fig. 2c), the chemical regime structure is similar to that for daily maxima. Relative to O_3^{max}, the VOC sensitive chemical regime extends

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further eastward over Germany and southward over France (Fig. 2d). For O_3^{moy}, the more VOC sensitive regime with respect to O_3^{max} is not surprising, because the target includes night time and morning ozone, which is more sensitive to titration by NO.

Next, we consider AOT40, AOT60, AOT90 values. As they are defined from con-
centration above threshold, spatial differences are expected to be more pronounced. AOT40 values (Fig. 2e) are strongest (40 000–70 000 ppb h for 12 summer months) over the Mediterranean basin and over Italy (>30 000–40 000). A strong land sea gradient in AOT40 is apparent which is due to low dry ozone deposition over sea as compared to larger values over land. The chemical regime with respect to AOT40 (Fig. 2f) has a similar spatial structure as that for O_3^{moy}. Note that changes over North-Western Europe (+3000–10 000 ppb h) are large as compared to the low absolute values in this region (10 000–15 000 ppb h).

AOT60 and AOT90 are largest for specific regions of strong emissions and pho-
tochemical activity in and around Italy (Po valley, bay of Genoa, . . . , Fig. 2g and i). In addition, AOT90 has secondary maxima over the Paris agglomeration and South-western Germany. For many more rural regions, AOT90 is near zero. Even though it has a more patchy structure, the chemical regime spatial distribution for AOT60 and AOT90 is again rather similar as for the previous indices (Fig. 2h and j): NO_x sensitive over Italy (with exception of notably parts of the Po valley) and in general the whole south – eastern part of the model domain, VOC sensitive over North-Western Europe, NO_x sensitive regime over South-Western Germany, but VOC sensitive over the Paris region. However, over Northern Germany, AOT60 is more NO_x sensitive than O_3^{max}. Finally, results for the SOMO35 also show a similar spatial structure (Fig. 2k and l).

This similarity in the spatial distribution in the chemical regime for different indices is an important result of this study, as it demonstrates the relevance of the chemical regime concept as well as the robustness of its application to Europe. Even though only a small number of days with particular conditions (low atmospheric circulation, clear sky) contribute to AOT90, the large-scale spatial structure remains similar to that of O_3^{max}, O_x^{max} and O_3^{moy}.

3.2 Relation to chemical regime indicators

In this section, we attempt to relate the average spatial structure of the chemical regime (for the case of O_3^{max}) to several explanatory factors, in particular to emission strength and accumulation, and to radical production and loss processes. This analysis is based on specific trace gas concentrations or ratios which have been widely used as so called "chemical regime indicators" in urban and urban plume studies (Milford et al., 1994; Sillman, 1995; and others).

As expected from theory (see Introduction), the chemical regime is more VOC sensitive in regions with large NO_x emissions (Fig. 3a), as especially over North-Western Europe (from Southern England to Western Germany), but also over parts of the Po valley, and the ship tracks in the Mediterranean Sea. NO_y has been proposed by Milford et al. (1994) as an indicator discriminating chemical regimes, because it is a tracer of NO_x emissions an air mass received during its recent history (hours to days). They found that a NO_y threshold value between 10 and 25 ppb separates the two chemical regimes for different polluted areas in US. Vogel et al. (1999) found threshold NO_y values between 6 and 13 ppb for South-Western Germany and discussed their variability with respect to the VOC/NO_x emission ratio, meteorological conditions and ozone advection.

In our study, large NO_y concentrations (Fig. 3b, average over summer 2001) are found in large emissions areas (for example Southern England) or in their lee (i.e. over the North Sea), or over ship tracks in the Mediterranean basin, where emission dispersion is low. NO_y concentrations fairly well correlate with the chemical regimes as depicted in Fig. 1d. The spatial correlation (R) between the chemical regime and NO_y concentrations, both averaged for summer 2001 at 15:00 UT, is 0.63, see Table 1). A threshold value of 7.6 ppb can be determined which optimally discriminates about 83% of the chemical regimes. This threshold value is at the lower end of the range of values given in the literature (see above), which can be explained by several reasons: (1) the lower VOC/NO_x emission ratio over Europe compared to US where biogenic

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VOC emissions are much larger (e.g. Curci et al., 2008), (2) a larger domain considered in our study making loss of the NO_y tracer through deposition more critical (i.e. NO_y is lost mainly through rapid HNO_3 deposition, while the chemical regime is still conserved, due to slower loss of ozone by dry deposition, thus information on the chemical regime is lost faster than the regime itself) and (3) consideration of average conditions in our study with lower ozone concentrations than in studies focussed on pollution episodes.

Our NO_y threshold value is larger in the southern part of the domain (∼9 ppb) than in the northern part of the domain (∼6 ppb). This is mainly due larger odd hydrogen radical ($HO_x=OH+HO_2+\sum RO_2$) production in the southern part of the domain, due both to larger radiation intensity and larger ozone concentrations.

The H_2O_2/NO_z ratio, also proposed as a chemical regime indicator by Sillman (1995), has proven useful, because it takes into account both the impact of emissions and radical production. It compares the time integrated radical sink through HO_x+NO_x reactions, yielding NO_z, to the time integrated radical sink through HO_x+HO_x recombination reactions, yielding H_2O_2. The latter corresponds to an excess radical production beyond titration with NO_x emissions, which favours a locally NO_x sensitive regime (Kleinman, 1997). Threshold values for this indicator are thought to be less dependent on ambient conditions, which has been verified for different European locations for the similar tracer H_2O_2/HNO_3 (Hammer et al., 2002). Fig. 3c shows low ratios over North-Western Europe and large ratios over most of the Mediterranean Sea, corresponding to the dominant chemical regimes in Fig. 1d (spatial correlation of −0.82, see Table 1). A threshold value of 0.205 optimally discriminates 89% of the chemical regimes. This threshold is at the lower end of a range of values given for five US agglomerations (between 0.23 and 0.41, Sillman et al., 1997).

Finally, the chemical regime trace gas ratio O_3/NO_z separates 81% of chemical regimes with a threshold value of 12.1 (spatial correlation −0.64). This is slightly larger than the range of values between 8 and 11 given by Sillman et al. (1997) and larger than the value of 6 to 7 found by Martilli et al. (2002) for a polluted episode in the Po valley (Milano plume). In conclusion, an important result of our study is that trace gas

ratios, that have been used to discern chemical regimes on an urban/regional scale during pollution episodes, are still useful on a larger, continental scale and for average summer conditions. Threshold values to distinguish chemical regimes found in this work are close to the range of values in the literature. In the next section, we will use the same trace gas ratios to understand the day to day variability of the chemical regime.

3.3 Inter-annual, seasonal, and day-to-day variability

In this section, we address the temporal variability of chemical regimes, on an inter-annual, seasonal and day to day scale. Differences between average results for summers 2001, 2002 and 2003 are rather weak, below 1 ppb in absolute terms and below 20% in relative terms for O_3^{max}. Largest deviations occur for summer 2003, due to the heat wave in August 2003, which will be examined below. Thus the restriction to analysis of a three-summer climatology appears to be justified for this work.

The monthly variability in the chemical regime from May to August is shown in Fig. 4, results for each month being averaged over years 2001–2003. Chemical regime distribution is fairly similar for different months. In May, the VOC sensitive regime is spatially slightly more extended over North-Western Europe, but maximum values in the London/Channel/Benelux region are lower ($<+5$ ppb, versus <7 ppb for the June to August period). In August, the NO_x sensitve regime is more pronounced over the Mediterranean basin (up to -5 ppb versus up to -3 ppb for the other months). These differences are not easy to explain. The more NO_x limited regime in the Mediterranean region in August is probably due to several effects: First, monthly climatologies derived from NCEP reanalysis (available at http://www.cdc.noaa.gov/cgi-bin/Composites/printpage.pl) indicate a temperature increase from May to August over the Mediterranean basin leading to lager specific humidity through evaporation. This in turn enhances radical production in the model through ozone photolysis, and results in larger simulated H_2O_2. Second, NO_x emissions in the model are smaller in August due to smaller emissions in the heating sector, and due to smaller agicultural soil emissions.

Both effects favour a more NO_x limited chemical regime in the Mediterranean basin.

August 2003 is a special case because anticyclonic blocking over Western Europe during the first half of the month allowed large heat and ozone build-up (e.g. Vautard et al., 2005). Different factors affect chemical regimes during this period in distinct ways: stronger emission accumulation ($\Rightarrow$more VOC sensitive regime), enhanced emission ageing due to longer residence times over Western Europe, larger biogenic VOC emissions due to enhanced temperature, enhanced radical production due to stronger enhanced actinic fluxes and ozone concentrations ($\Rightarrow$more NO_x sensitive regime), enhanced photochemical ozone build-up (larger overall sensitivity to local emissions). Figure 5a shows that the chemical regime spatial distribution in August 2003 is similar to that in August 2001–2003 (Fig. 4d), but with gradients between chemical regimes enhanced. Thus the interplay between these different factors makes chemical regimes more pronounced, but does not change their general structure. For AOT90, results for August 2003 (Fig. 5b) are much similar to those for the whole period (Fig. 2j), because most of exceedence of the 90 ppb level occurred during August 2003.

We now analyse the day-to-day variability in the chemical regime induced by changes in meteorological conditions. For this, we average the chemical regime, here with respect to O_3^{max}, for individual days over all grid points within three specific regions:

- the Mediterranean region (6° W–20° E, 38° N–43° N, MED) with an average NO_x sensitive chemical regime,

- Northern-Eastern Germany 9° W–14° E, 50° N–54° N, NEG) with an average near neutral regime,

- the region in North-Western Europe with a pronounced VOC sensitive regime (1° W–6° E, 50° N–53° N, NWEU).

Figure 6 shows the daily variability of the chemical regimes for these regions (always at 15:00 UT): always VOC sensitive for NWEU, but with a high variability (+1 ppb < D_O_3<+9 ppb), always NO_x sensitive for the MED (−3.5 ppb<D_O_3<−0.5 ppb), and

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variable for NEG ($-7\,\text{ppb} < D\_O_3 < +4\,\text{ppb}$). Chemical regime tracers introduced in Sect. 3.2 are now calculated for each day (at 15:00 UT) and related to the chemical regime. From Fig. 6b–d, it can be seen that ranges of values for indicators are distinct for different regions. This is expected from the strong spatial differences in the summer average indicator values presented in Sect. 3.2 corresponding to the different chemical regimes. As for the average chemical regime, the H_2O_2/NO_z indicator shows more skill than the O_3/NO_z indicator and the NO_y indicator for NEG and MED, as illustrated by larger temporal correlation coefficients (Table 2). This is in agreement with the most physically relevant formulation of the H_2O_2/NO_z indicator outlined in Sect. 3.2. Also regional differences appear, for instance the $O3/NO_z$ and the NO_y indicators show distinctive skill only for NWEU, but not for NEG and MED. NWEU is characterised by strong and fresh NO_x emissions and thus the NO_y indicator is more relevant there than over NGE and MED where NO_y concentrations are due to older emissions giving rise to more loss of information by dry deposition.

When studying the chemical regime daily variability, we would like to know if days with high ozone concentrations are related to a particular chemical regime different from average. Our results show that for NWEU, the chemical regime is independent of daily ozone maxima, for MED it is slightly more NO_x sensitive for large ozone values and for NEG it is strongly more NO_x sensitive for large ozone values (Fig. 6a). Thus for large ozone values, relevant for air quality issues, the chemical regime is NO_x sensitive over NEG. Correspondingly the NEG chemical regime is also slightly NO_x sensitive with respect to AOT60, a target which gives larger weight on high ozone values (Fig. 2h). This behaviour can be tentatively explained as follows: enhanced ozone values trigger enhanced radical production by ozone photolysis, shifting the chemical regime to more NO_x sensitive. For NWEU, ozone and NO_y are correlated (as can be expected for near source regions), larger NO_y and NO_x values be indicative and favouring a more VOC sensitive chemical regime. Thus, for NWEU there are two compensating effects and the chemical regime is finally independent of O_3 levels (Fig. 6a). For NEG and MED, regions where NO_x and NO_y levels are due to older emissions, NO_y is not a valid

chemical regime indicator as we have seen before (Fig. 6b). Correspondingly, there is no compensating effect, and thus a more NO_x sensitive chemical regime is realised for larger ozone concentrations.

As a conclusion, we have shown in this section that indicator species can be used to explain the daily variability of the chemical regime in terms of NO_x emissions and radical production. Differences in skill of indicators within different regions are apparent; Also the relation of the chemical regime with respect to ozone concentrations differs from one region to another as a function of the remote or polluted character of a region.

3.4 Decadal variability with respect to European emission changes

In this section, we address the impact of estimated past and future emission changes on the chemical regime over Europe. Simulations with summer 2001 meteorology (the summer season that gives results closest to the 2001–2003 average) have been performed for years 1980, 1990, 2010 and 2020 emissions and are compared to the reference simulations with year 2002 emissions. All emissions sets have been taken as expert emissions from the EMEP/Webdab site (http://www.ceip.at/, Vestreng et al., 2005). Emissions for 2010 and 2020 are projections. The same boundary conditions are used for all cases in order to isolate the regional signal. The chemical regimes resulting from these emission data sets are shown in Fig. 7 for the case of O_3^{max}. The most striking feature is the change in magnitude of the VOC sensitive regime over the Southern UK/Channel/Benelux/Rhine-Ruhr region, values decreasing from more than +15 ppb for 1980 and 1990 to less than +5 ppb for 2010 and 2020. For Germany, a general switch form a VOC sensitive regime in 1980 and 1990 to a NO_x sensitive regime in 2010 and 2020 can be noted. On the contrary, changes in the intensity in the NO_x sensitive regime over the Mediterranean basin are only minor. For AOT60 (not shown), the same type of evolution is found, the VOC sensitive regime being much less pronounced in 2010/2020 than in 1980/1990 and the regime shifting from VOC to NO_x sensitive over Germany. Very low AOT90 is simulated for the years 2010 and 2020, which makes it difficult to use AOT90 as a target for future chemical regime

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analysis. These changes can be related to the emission changes summarized in Table 3. For United Kingdom, the Benelux, Germany and France, anthropogenic NO_x and NMVOC emission reductions especially between 1990 and 2010 are very large, reaching about a factor two to three, resulting in the large simulated decrease in VOC sensitivity over that area. Emission changes in the periods 1980 to 1990 and 2010 to 2020 are in general much lower than those between 1990 and 2010, thus the major changes in chemical regimes occur between 1990 and 2010. As a conclusion, there is a clear tendency towards a more NO_x sensitive chemical regime over Europe over time, consistent with ongoing NO_x emission reductions.

4 Impact of model uncertainty

In this section, the robustness of simulated chemical regime structure with respect to possible model uncertainty is evaluated. Even if comparison with observations made in previous studies (see Sect. 2) showed rather small model errors in particular for daily ozone maxima, the model sensitivity with respect to emission changes cannot directly be assessed from comparison with observations. Ideally, this problem could be addressed by applying Monte Carlo analysis, which allows taking into account the global model uncertainty. This type of analysis has been performed for the Greater Paris region and it could be shown that the average VOC sensitive regime found over this area was robust with respect to model uncertainties in emissions, meteorological and kinetic data (Beekmann and Derognat, 2003; Deguillaume et al., 2008). However, on a continental scale such an analysis is more difficult to perform, because uncertainties are more difficult to represent with such methods, as perturbations cannot be taken as uniform across the domain (which was the case in the previous local studies). Taking into account a spatial structure for the perturbations would make the number of simulations very large. In the present work, the evaluation of model robustness is simply made by performing a small number of well chosen sensitivity simulations:

1. Anthropogenic VOC emissions are increased by 40%; indeed, chemical regimes

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are sensitive to the VOC/NO$_x$ emissions ratio. Modified VOC emission also mimic uncertainties in the photochemical reactivity of the gas phase chemistry scheme.

2. The reduced MELCHIOR gas phase mechanism (40 compounds, ~120 reactions, Schmidt et al., 2001) was replaced by the extended one (~80 compounds, 320 reactions, Lattuati, 1997).

3. Simulations were analysed in the second model layer (50–200 m height) instead of the first layer (0–50 m height); differences in results indicate the presence of complex vertical structures with low mixing which might be difficult to be resolved by the model.

For all these configurations, a reference and two reduction scenario simulation are carried out in order to calculate the chemical regime as above. Simulations only cover the month of June 2002 and results are displayed in Fig. 8. For all configurations the gross structure in the chemical regime with respect to O$_3^{max}$ and AOT90 (not shown) remains the same as for the standard configuration. For the increased VOC emission case, maximum values within the VOC sensitive regime are in the range of 7–10 ppb instead of 5–7 ppb for the reference case. At first sight this is not consistent with theory, which predicts that regions with enhanced VOC/NO$_x$ emission ratio should be more NO$_x$ sensitive (Kleinman et al., 1997; Sillman, 1999). An enhanced initial VOC/NO$_x$ ratio in this region triggers enhanced photochemical ozone production (not shown) which actually leads to a more positive value for the chemical regime, which anyway is strongly VOC sensitive. The simulations with the extended and reduced chemical mechanism yield almost identical results (differences in general below half a ppb). The chemical regime in model layer two is very similar to that in the surface layer over continental areas. Indeed, mixing between these two layers in the afternoon and under summer conditions is strong in most cases. However, large differences can be found in coastal areas. VOC sensitive chemical regimes apparent in the surface layer especially near coastal pollution sources disappear in the second model layer (for example over the Adriatic sea, between Genoa and Corsica). Over the ship tracks near the North African coast, the

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VOC sensitive regime is less pronounced in model layer two than one. This behaviour is due to suppressed vertical mixing over water surfaces, which keep emissions concentrated near the ground, thus leading to a VOC sensitive regime there. However, the uncertainty of these results with respect to simulated vertical mixing is much stronger than that over continental areas, because few observational data exist to verify this complex vertical structure. Differences in the chemical regime with respect to AOT90 show the same behaviour than those for O_3^{max}.

As a conclusion to this part, the similarity of chemical regimes for these different sensitivity tests, with the exception of VOC sensitive regimes over the Mediterranean sea, is an important result, because it shows that the chemical regime simulations are robust with respect to model uncertainties (at least those taken into account which are believed to represent model uncertainty with respect to chemical regimes).

5 Conclusions

In this work, the robustness and time variability of chemical regimes over Europe during summers 2001 to 2003 has been analysed based on regional scale CTM simulations. A VOC sensitive regime over North-Western Europe (over Southern UK, the Channel region, and parts of the North Sea, the Benelux, Northern France and Western Germany) and a NO_x sensitive regime over the Mediterranean basin and over Eastern Europe, with exception of ship tracks and several large agglomerations (i.e. Barcelona , Milano), are found. Over Northern Germany, the chemical regime is near neutral. This confirms earlier work by Tarasson et al. (2003) and Derwent (2003). Then, time variability and robustness, with respect to environmental factors and model uncertainty, of this chemical regime structure has been systematically analysed. First, the spatial distribution of chemical regimes is rather unchanged with respect to the ozone target considered: daily maximum ozone or O_x (sum of O_3 and NO_2), daily mean ozone, AOT40, AOT60, AOT90 and SOMO35. Only over Northern Germany, the chemical regime can shift from either slightly VOC sensitive (for daily mean ozone, AOT40, SOMO35) to

slightly NO_x sensitive (for daily max. O_x, AOT60). Chemical regimes appear also robust over various time scales: year to year, month to month, day to day. During August 2008, when Western Europe was affected by an exceptionally hot and anticyclonic period, the chemical regime structure remains unchanged, but differences between VOC and NO_x sensitive regions are more pronounced. Chemical regimes are variable from one day to the other, but always remain VOC sensitive over North-Western Europe and NO_x sensitive over the Mediterranean basin.

Emission strength is one of the known key factors determining the occurrence of a chemical regime. We find that the chemical regime strongly responds to past or projected emission changes over Europe between 1980 and 2020. The magnitude of the VOC sensitive regime over North-Western Europe decreases from more than +15 ppb for 1980 and 1990 to less than +5 ppb for 2010 and 2020. For Germany, a general switch form a VOC sensitive regime in 1980 and 1990 to a NO_x sensitive regime in 2010 and 2020 is simulated, while for the Mediterranean basin changes are minor. As a conclusion, there is a clear decadal tendency towards more NO_x sensitive regimes over Europe.

The robustness of chemical regimes with respect to model uncertainty (in emissions, chemistry, vertical transport) has also been assessed. For all configurations the gross structure in the chemical regime remains unchanged. However, uncertainty in vertical transport is expected to affect the chemical regime over water surfaces in the Mediterranean Sea.

The use of indicator species proposed in the literature to predict chemical regimes in particular for pollution episodes has been extended here to a larger spatial and temporal scale. It could be shown that NO_y, H_2O_2/NO_z and O_3/NO_z ratios show distinctive skill for the structure of the summer averaged chemical regime over Europe. They are also correlated with the chemical regime temporal variability, to a different extent for different regions. Use of these indicators allows explaining the spatio-temporal regime variability in terms of variability in emission strength and radical production.

This study aimed at exhibiting regional scale patterns of chemical regimes which are

still resolved in a continental scale simulation with a 0.5° horizontal resolution. But finer urban scale features could not be addressed here, for computer time and memory size reasons it was not possible to perform European wide simulations with high enough resolution (about 5 km, Thunis et al., 2007) to resolve such features. However, progress in computer capacities might allow such type of simulations in future.

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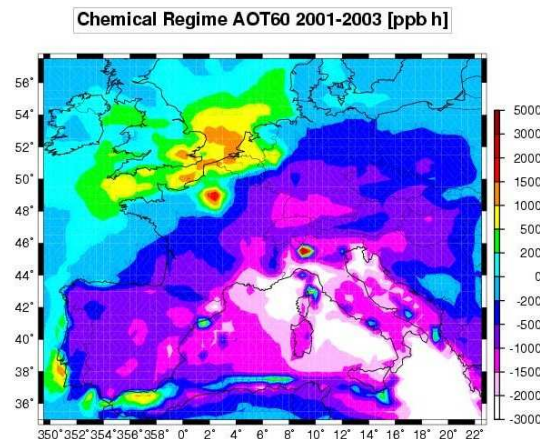
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Table 1. Relations between chemical regimes and indicators, averaged over summer (May–August) 2001 at 15:00 UT.

	H_2O_2/NO_z	O_3/NO_z	NO_y [ppb]
Spatial correlation with chemical regime	-0.82[a]	-0.64[a]	0.63
Threshold value	0.205	12.1	7.6
(literature values in parenthesis)	(0.23–0.41)	(6–11)	(6–25)
Discriminative capacity	89%	81%	83%

[a] Values indicate correlation coefficients with the negative of inverse of the indicator, in order to obtain a near linear relation with the chemical regime.

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Table 2. Temporal correlation (R) between chemical regimes and indicators at 15:00 UT during summer (May–August) 2001.

Region	H_2O_2/NO_z	O_3/NO_z	NO_y [ppb]	O_3 [ppb]
NW Europe	-0.72^a	-0.82^a	0.71	0.21
NE Germany	-0.80	-0.17	0.30	-0.75
Mediterranean Basin	-0.65	-0.15	0.04	-0.52

[a]Values indicate correlation coefficients with the negative of inverse of the indicator, in order to obtain a near linear relation with the chemical regime.

Table 3. NO_x and VOC emissions and emission projections for selected countries from http://www.ceip.at/ (Vestreng, 2005).

Country	NO_x emissions Gg O_2 equivalents					NMVOC emissions Gg				
	1980	1990	2002	2010	2020	1980	1990	2002	2010	2020
UK	2580	2771	1578	1113	802	2100	2420	1166	901	863
Benelux[a]	1023	911	671	552	454	853	763	460	409	416
Germany	3333	2844	1492	1174	905	3223	3590	1491	1140	867
France	2024	1897	1275	1051	812	2733	2499	1475	1024	937
Italy	1585	1918	1267	980	669	2032	1992	1343	971	732
Spain	1068	1206	1420	924	668	1392	1591	1090	832	794

[a]Here the sum of emissions for Belgium and the Netherlands is taken.
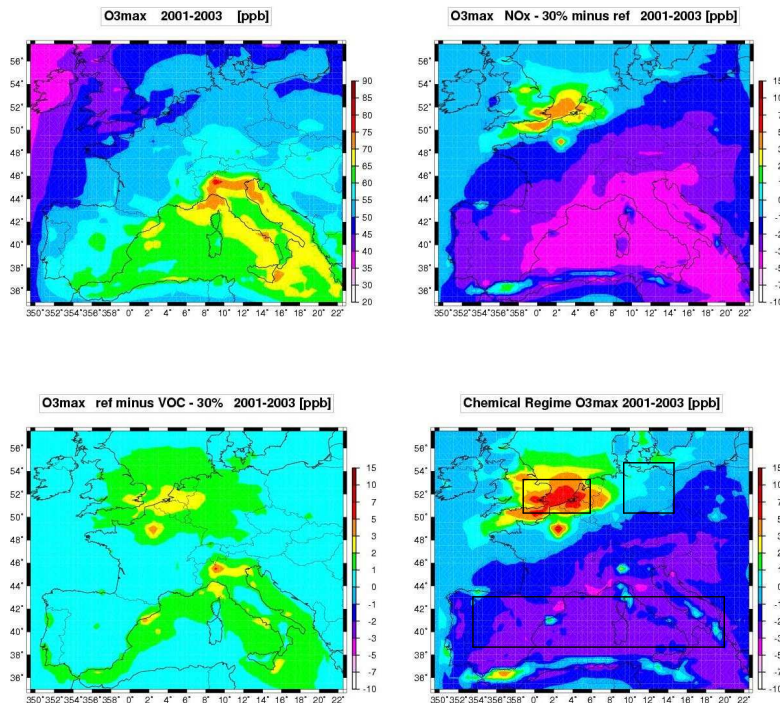
Fig. 1. Reference simulation and reduced emission simulations for average daily ozone maxima for three summers (May to August) 2001–2003; **(a)** reference simulation, **(b)** difference between 30% reduced anthropogenic NO_x emission and reference scenario, **(c)** difference between reference and 30% reduced anthropogenic VOC emission and reference scenario, **(d)** chemical regime map: difference between a 30% reduced NO_x and a 30% reduced VOC emission scenario. Note that differences between the scenario run and the reference are inverted in (c) with respect to (b), because this allows simply adding (b) and (c) in order to obtain the chemical regime. (d) also shows delimitations of the three domains over North-Western Europe, over North-Eastern Germany and over the Mediterranean basin that will be used for analysis of the chemical regime temporal variability (see Fig. 6).
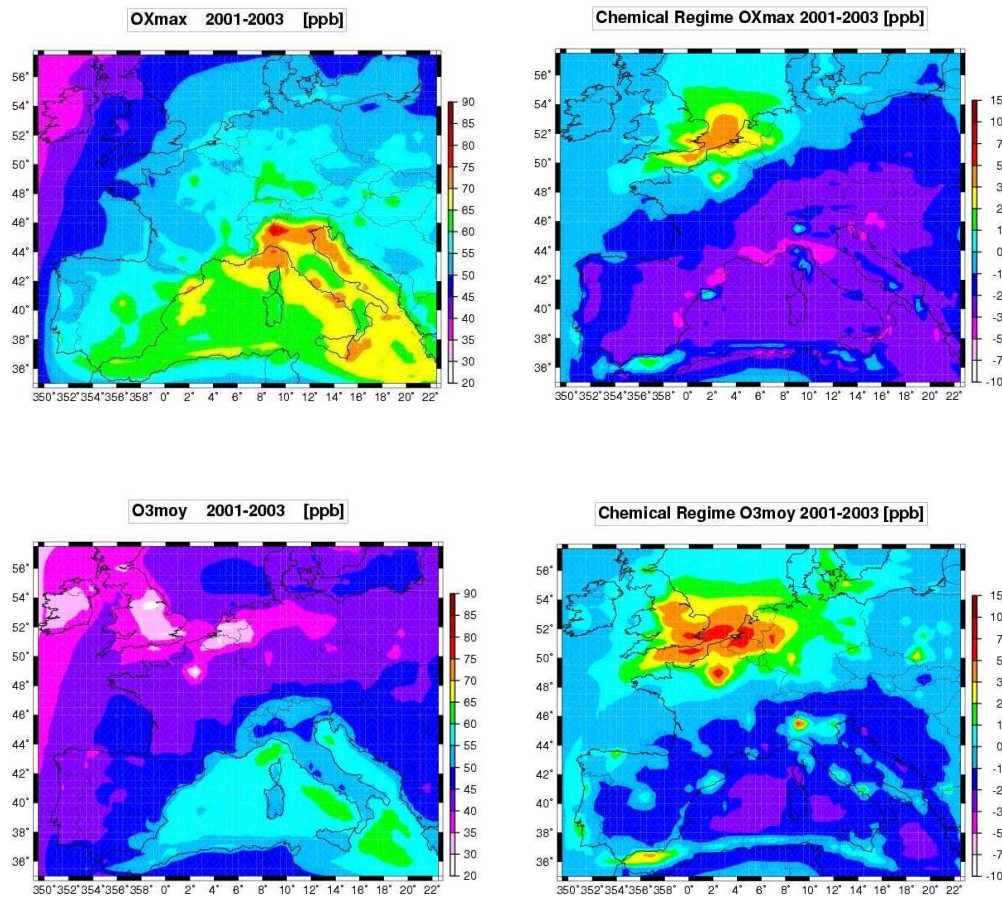
Fig. 2a–d. Reference and chemical regime simulations for different ozone targets (period as in Fig. 1): **(a, b)** daily O_x (=O_3+NO_2) maximum, **(c, d)** daily mean ozone; for definition of AOT's and SOMO35 see explanation in the text.
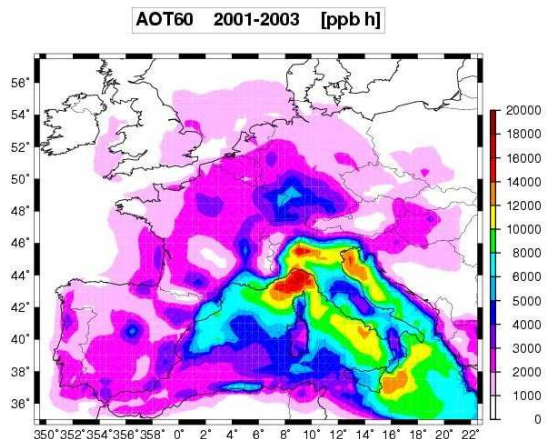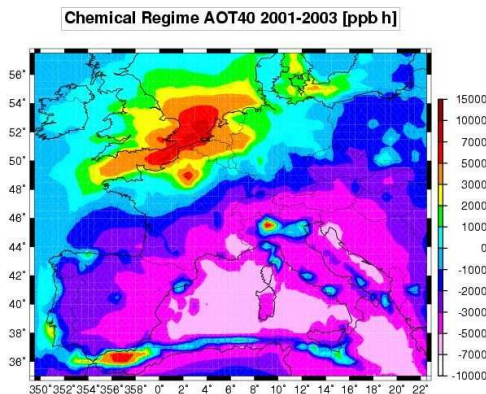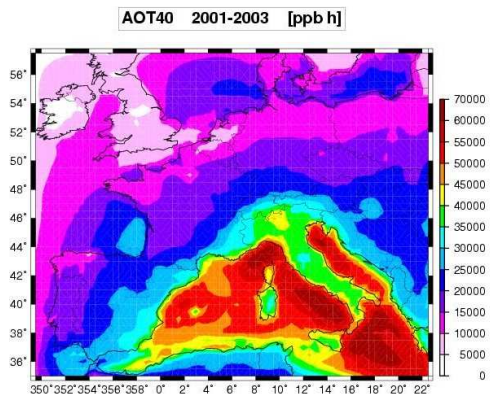
Fig. 2e–h. Reference and chemical regime simulations for different ozone targets (period as in Fig. 1): **(e, f)** AOT40, **(g, h)** AOT60; for definition of AOT's and SOMO35 see explanation in the text.
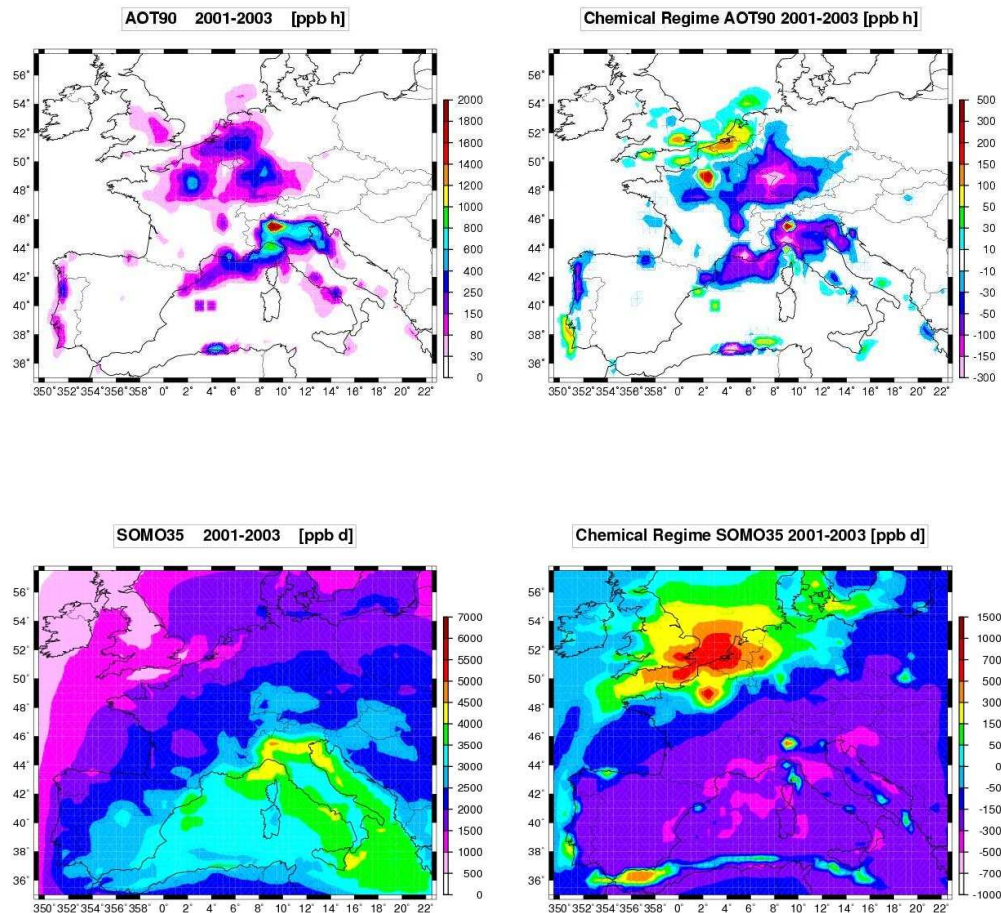
Fig. 2i–l. Reference and chemical regime simulations for different ozone targets (period as in Fig. 1): **(i, j)** AOT90, **(k, l)** SOMO35; for definition of AOT's and SOMO35 see explanation in the text.
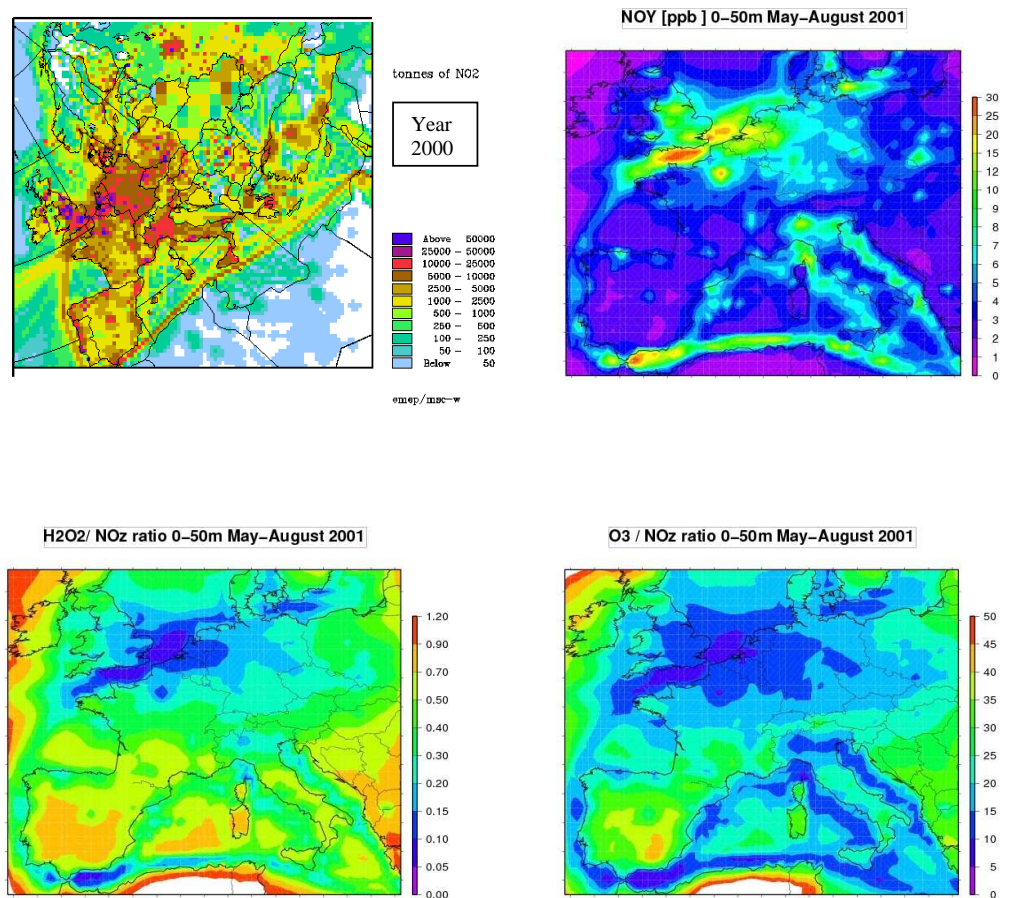
Fig. 3. Maps of annual NO_x emissions (NO_2 equivalent) for year 2000 per $50 \times 50 \, km^2$ grid cells **(a)**, chemical regime indicator concentration or rations (averaged over summer 2001): **(b)** NO_y [ppb], **(c)** H_2O_2/NO_z ratio, **(d)** O_3/NO_z ratio.
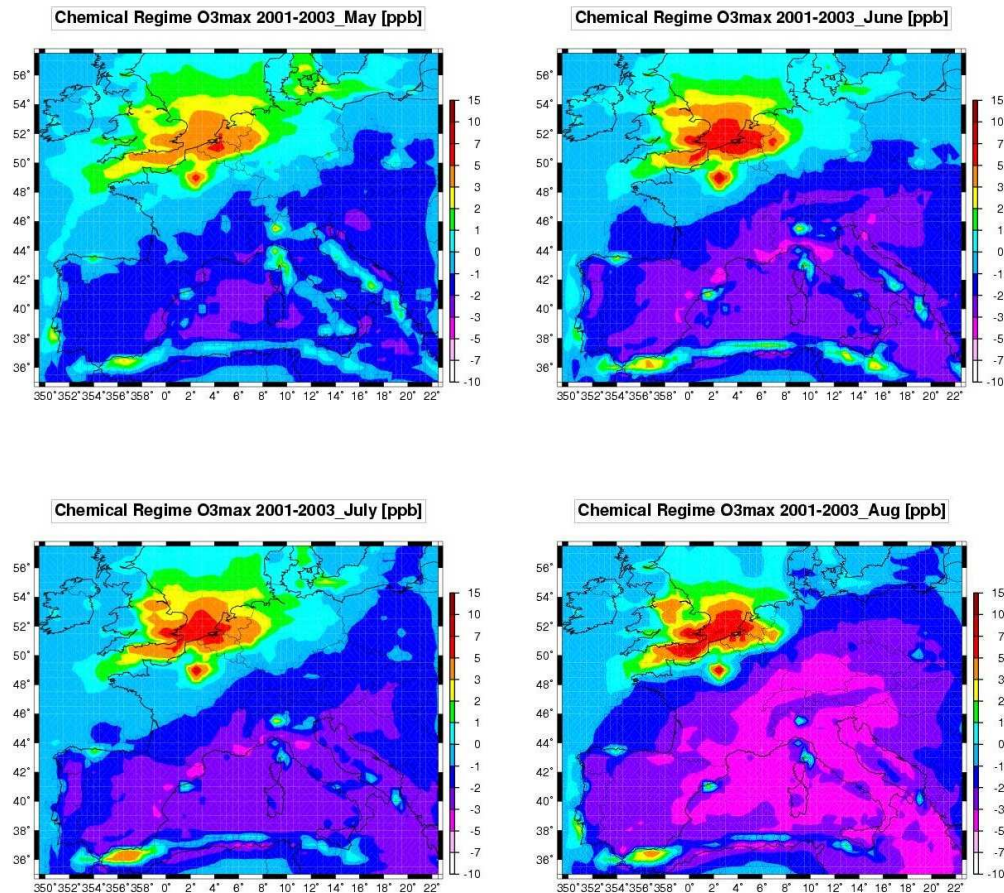
Fig. 4. Average chemical regime (with respect to daily ozone maximum) for **(a)** May, **(b)** for June, **(c)** for July, **(d)** and for August 2001–2003.

Chemical regimes over Europe

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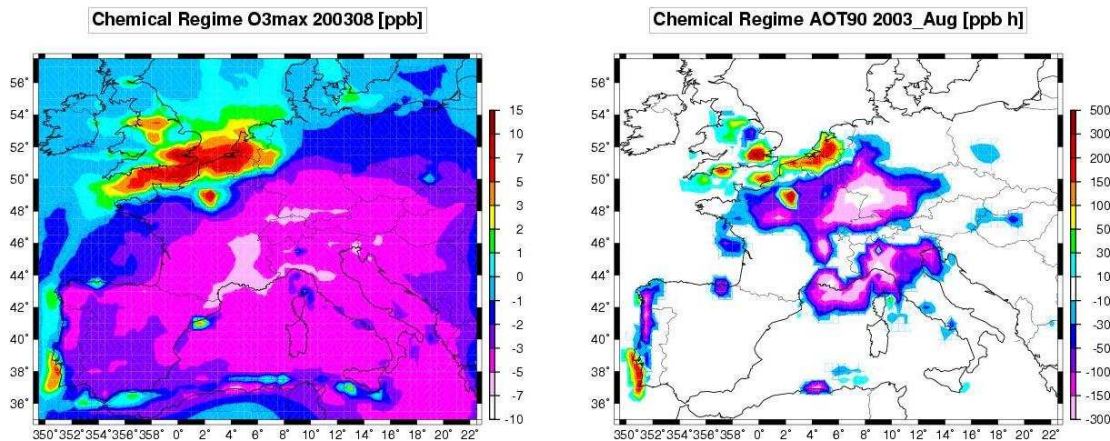
Fig. 5. Chemical regime simulations for August 2003: **(a)** chemical regime for daily ozone maximum, **(b)** chemical regime for AOT90.
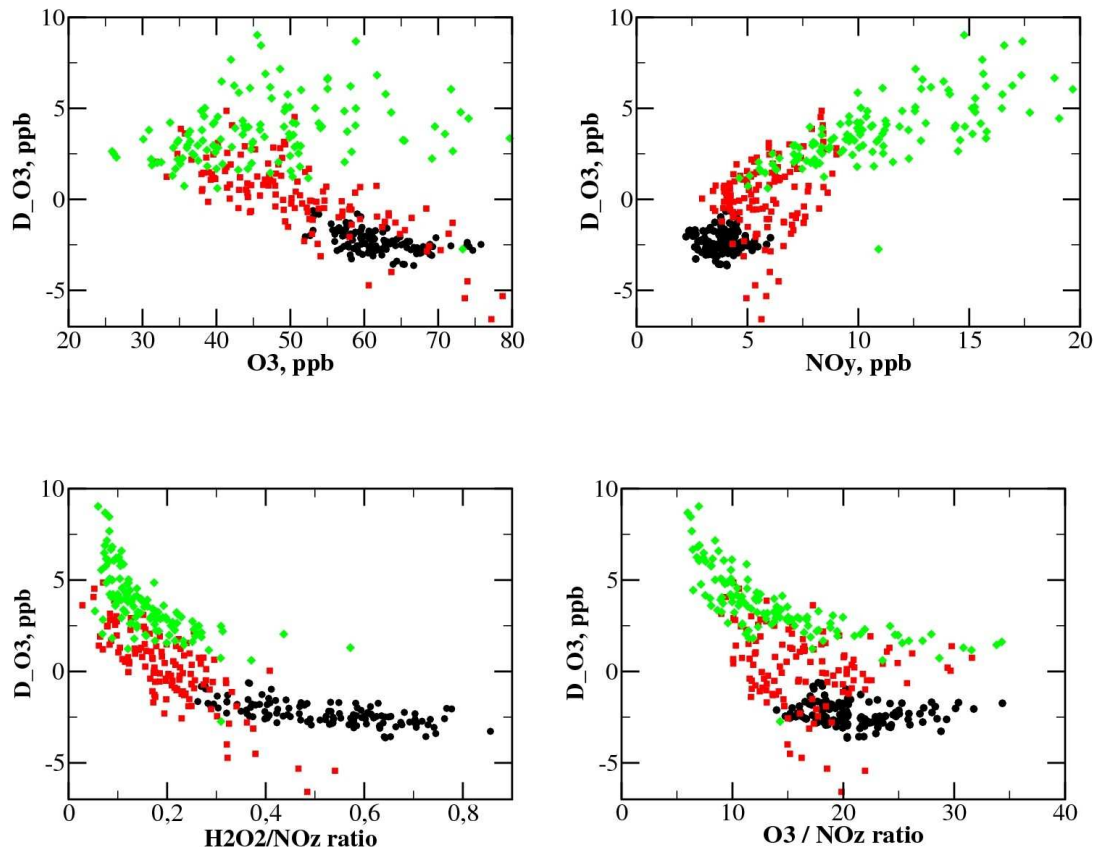
Fig. 6. Scatter plots of chemical regime (at 15:00 UT [ppb]) versus regime indicators: **(a)** 15:00 UT ozone [ppb], **(b)** 15:00 UT NO_y [ppb], **(c)** 15:00 UT H_2O_2/NO_z ratio, **(d)** 15:00 UT O_3/NO_z ratio. Black circles indicate averages for the Mediterranean area (6° W–20° E, 38° N–43° N), red squares for North-Eastern Germany (9° E–14° E, 50° N–54° N), green diamonds for North-Western Europe (1° W–6° E, 50° N–53° N). Figure 1d shows the locations of the three domains.
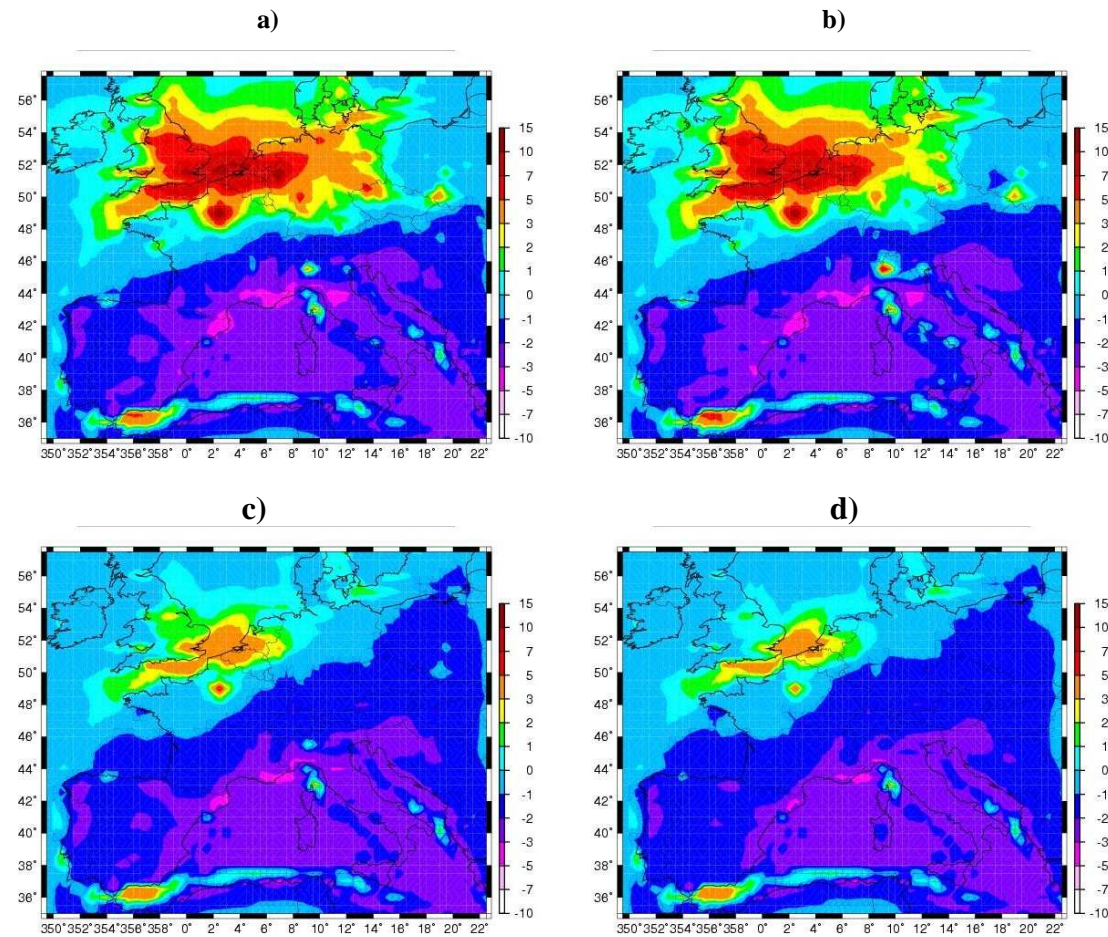
Fig. 7. Chemical regime simulations with respect to daily ozone maximum for summer 2001 meteorology, but for **(a)** 1980, **(b)** 1990 emissions, **(c)** 2010, **(d)** 2020 emission projections.

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Interactive Discussion
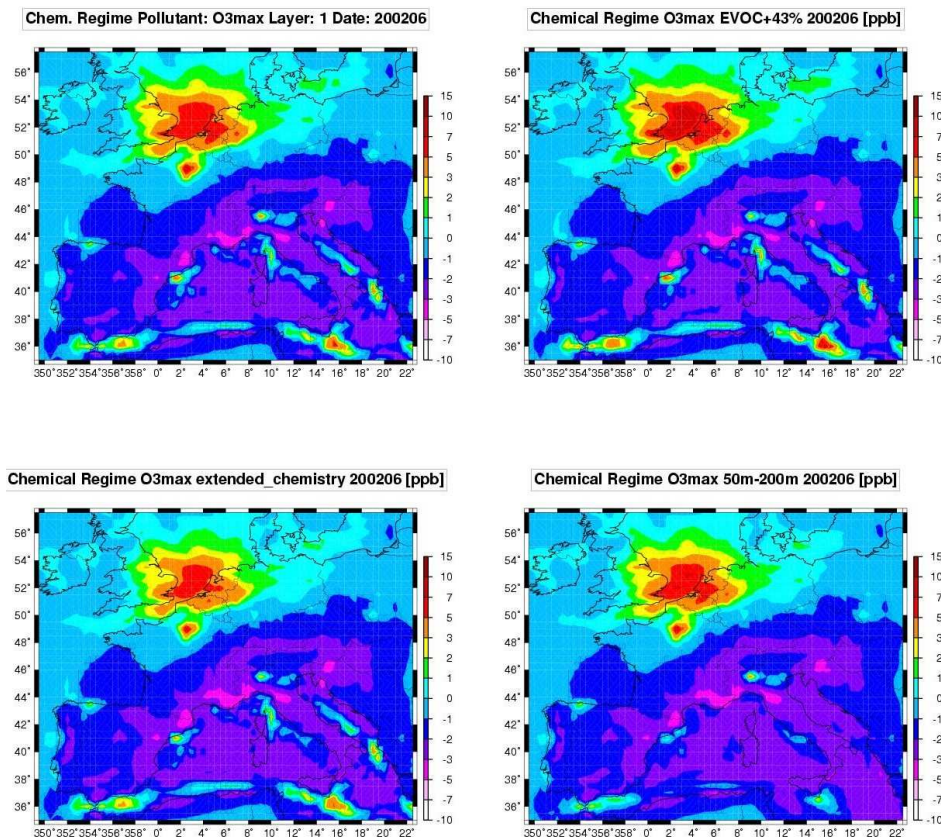
Fig. 8. Sensitivity of chemical regime simulations with respect model configuration and input data (for June 2002 and with respect to daily ozone maximum): **(a)** reference, **(b)** with anthropogenic VOC emissions increased by 40%, **(c)** with the extended MELCHIOR chemical mechanism instead of the reduced one, **(d)** results analysed in model layer 2 (50–200 m height) instead of layer 1 (0–50 m height).