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Modelling study of the impact of isoprene and terpene biogenic emissions on European ozone levels

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ABSTRACT

The impact of biogenic volatile organic compound (BVOC) emissions on European ozone distributions has not yet been evaluated in a comprehensive way. Using the CHIMERE chemistry-transport model the variability of surface ozone levels from April to September for 4 years (1997, 2000, 2001, 2003) resulting from biogenic emissions is investigated. It is shown that BVOC emissions increased on average summer daily ozone maxima over Europe by 2.5 ppby (5%). The impact is most significant in Portugal (up to 15 ppby) and in the Mediterranean region (about 5 ppbv), being smaller in the northern part of Europe (1.3 ppbv north of 47.5°N). The average impact is rather similar for the three summers (1997, 2000, 2001), but is much larger during the extraordinarily hot summer of 2003. Here, the biogenic contribution to surface ozone doubles compared to other years at some locations. Interaction with anthropogenic NO_x emissions is found to be a key process for ozone production of biogenic precursors. Comparing the impact of the state-of-the-art BVOC emission inventory compiled within the NatAir project and an earlier, widely used BVOC inventory derived from Simpson et al. [1999. Inventorying emissions from nature in Europe. Journal of Geophysical Research 104(D7), 8113-8152] on surface ozone shows that ozone produced from biogenic precursors is less in central and northern Europe but in certain southern areas much higher e.g. Iberian Peninsula and the Mediterranean Sea. The uncertainty in the regionally averaged impact of BVOC on ozone build-up in Europe is estimated to be $\pm 50\%$.

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1. Introduction

Biogenic volatile organic compounds (BVOCs) play an important role in fuelling the photochemistry of polluted boundary layer and may contribute significantly to severe ozone events (e.g. Solmon et al., 2004). However, despite the efforts put in setting up accurate biogenic emission inventories, uncertainties in European scale biogenic emission estimates remain large, with a factor of 3–5 for key species such as isoprene (Simpson et al., 1999; Table 26). In consequence, conclusions drawn on the impact of BVOC on atmospheric chemistry are rather vague. In this context, the EU/FP6 Natural and Biogenic Emissions and Assessment of Impacts on Air Quality (NatAir project, http://natair.ier.uni-stuttgart.de/) aims at collecting latest research results on all relevant pollutant emissions from natural and biogenic sources in Europe and integrating them into new inventories. Here we present the first continental scale modelling evaluation of the long-term



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impact on surface ozone levels resulting from biogenic isoprene and terpenes using a new temporally and spatially highly resolved emission estimates developed within the NatAir project.

Global emissions of non-methane volatile organic compounds (VOCs) from vegetation account for about 1150 million tonne carbon per year ($TgCyr^{-1}$; Guenther et al., 1995), corresponding to about 90% of total VOC emissions including anthropogenic sources. Among biogenic emissions, isoprene and terpenes are the most abundantly emitted species and forested areas are the most important sources. Once in the atmosphere, oxidation of these VOCs produces variable amounts of ozone and secondary organic aerosol, depending in particular on the presence of nitrogen oxides (Atkinson and Arey, 2003). Thus, these products affect both air quality and climate. Modelling of BVOC emissions is complicated by their great sensitivity to environmental parameters (mainly temperature and radiation), vegetation type and leaf area (Guenther et al., 1995), making them very sensitive to climate and land use changes (Lathière et al., 2006; Purves et al., 2004). In a recent modelling study, von Kuhlmann et al. (2004) show that based on different modelling scenarios the uncertainty of the overall effect of isoprene on the global tropospheric ozone burden ranges between -35% and +35%, with much larger local variations.

In Europe, in contrast to the global picture, emissions of VOC from anthropogenic sources (AVOC) are higher than biogenic sources on an annual basis and at continental scale (Simpson et al., 1999), but the situation varies from country to country (e.g. in France AVOC are twice BVOC emissions, in Spain and Portugal AVOC≈BVOC) and season to season (e.g. in summer in Germany BVOC>AVOC; Steinbrecher and Koppmann, 2007). Biogenic VOC emission factors and their seasonal variation have been refined for some characteristic plants in specific regions of Europe on the basis of recent published literature, in particular within the Mediterranean area and northern Europe (for references see Steinbrecher et al., 2008).

Early estimates suggested a minor impact of biogenic isoprene emissions on April–September mean ozone levels at continental scale (Simpson et al., 1999). However, several later modelling studies, carried out at a more local/regional scale in the frame of field campaigns, pointed out the important role of biogenic emissions even in an urbanized landscape during specific air pollution events (Thunis and Cuvelier, 2000 for Burriana region (Spain); Duane et al., 2002 for Insubria (Northern Italy); Derognat et al., 2003 for the Ile de France region; Solmon et al., 2004 for Northern France; Sotiropoulou et al., 2004 for the Greater Athens and Marseille region; Liu et al., 2007 for Po Valley). One of the key features from these campaigns is that abundant anthropogenic NO_x sources in some of these areas boost the oxidation of highly reactive BVOCs (Barket et al., 2004), so that the episodic contribution to ozone production from biogenic sources could be as high as 50–75% in Northern Italy (Duane et al., 2002). Further, the sensitivity to emissions is shifted towards a more "NO_x-limited" regime (Derognat et al., 2003; Sillman et al., 2003), with important implications for emissions abatement strategies.

Here we investigate the impact of biogenic emissions on ozone at European scale with high spatial and temporal resolution. We present results of simulations of the April-September period for the 4 years (1997, 2000, 2001, 2003) for which NatAir biogenic isoprene and terpene emissions were calculated on hourly basis for $10 \times 10 \text{ km}^2$ cells. The main aim is a long-term inter-annual evaluation of the impact of biogenic VOC emissions on ozone levels over Europe. Such kind of long-term assessment at continental scale has not yet been performed so far. We also report on the differences between the new NatAir inventory and the one implemented by default in the CHIMERE model (Derognat et al., 2003), because the latter one is based on the widely used inventory by Simpson et al. (1999). In Section 2 we describe the CHIMERE modelling system and biogenic emissions used. In Section 3 we show results of simulations. Related uncertainties are discussed in Section 4. Concluding remarks and an outlook are given in Section 5.

2. Approach/method

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) in its version V200606A (see http://euler.lmd. polytechnique.fr/chimere/), modified here to include detailed NatAir biogenic VOC emissions for an extended European area. The model has been applied to simulate and analyse pollution episodes at continental (Vautard et al., 2005; Hodzic et al., 2006) and regional scale (Monteiro et al., 2007; Coll et al., 2005; Derognat et al., 2003), for longterm ozone trends analysis (Vautard et al., 2006) and for diagnostics or inverse modelling of emissions (Vautard et al., 2003; Deguillaume et al., 2007; Konovalov et al., 2007). The model has also been used for experimental (Blond and Vautard, 2004) and operational forecast of pollutant levels over Western Europe (Honoré et al., 2007; http://www.prevair.org). It is designed to simulate both the gaseous and the aerosol phase (Bessagnet et al., 2004), but here we will focus on the gas phase only. The model is set up on a $0.5^{\circ} \times 0.5^{\circ}$ horizontal grid covering all Europe ([35– 70°N; 15°W–35°E]) and eight hybrid-sigma vertical layers extending to 500 hPa.

Meteorological input is provided by PSU/NCAR MM5 model (Dudhia, 1993) run at $48 \times 48 \text{ km}^2$ horizontal resolution and 33 vertical sigma layers extending up to 100 hPa, and was regridded on the $0.5^{\circ} \times 0.5^{\circ}$ CHIMERE grid. The model is forced by ECMWF ERA-40 reanalysis taken at $1.125^{\circ} \times 1.125^{\circ}$ using the grid nudging (grid FDDA) option implemented within MM5.

Anthropogenic emissions are derived from EMEP annual totals scaled to hourly emissions applying temporal profiles provided by IER (Friedrich, 1997), as described in Schmidt et al. (2001). VOC emissions are aggregated into 11 model classes following the mass and reactivity weighting procedure proposed by Middleton et al. (1990). Biogenic emissions are described in the following subsection.

The gas-phase chemical mechanism MELCHIOR (Lattuati, 1997) includes about 80 species and more than 300 reactions. Isoprene oxidation is derived from the work of Paulson and Seinfeld (1992), with modifications to the fate of isoprene nitrates (see Section 4). α -Pinene is chosen as a representative for terpenes and its oxidation pathway is based on that included in the RACM mechanism (Stockwell et al., 1997).

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).

2.2. Biogenic volatile organic compound emissions

Here we give a brief description of the two biogenic VOC inventories used in this study and compare differences in the calculated emissions. In the standard version used in CHIMERE, biogenic emissions are calculated online as described by Derognat et al. (2003), hereafter referred to as D03. For isoprene and light-dependent terpene emissions, the algorithm is based on the widely used parameterization by Guenther et al. (1995) with the flux of VOC *i*:

$$F_i = \epsilon_i D\gamma_i \tag{1}$$

modelled as a function of emission potential ε_i , foliar density *D* specific for European vegetation (Simpson et al., 1999) and environmental correction factor γ_i , that accounts for temperature and radiation dependence, after Guenther et al. (1995).

Alternatively, biogenic VOC emissions have been calculated with a specific model described by Steinbrecher et al. (2008) based on a approach used for estimating BVOC emissions from Germany (Smiatek and Steinbrecher, 2006). This model (hereafter referred to as "NatAir" model) is more detailed than the D03 model in several respects:

- (1) use of plant species distributions on a regional level instead of general distributions on national level,
- (2) revised emission factors and biomass densities, including their seasonal variability,
- (3) introduction of a canopy model to adjust for light extinction and the leaf temperature variations inside the canopy, please refer to Steinbrecher et al. (2008) for further details.

NatAir BVOC emissions have been calculated hourly on a $10 \times 10 \text{ km}^2$ grid for the years 1997, 2000, 2001 and 2003 using meteorological fields simulated with the MM5 model after regridding the output to the required mesh size. It has been verified that simulations with different resolutions lead to globally consistent meteorological fields, showing only episodic local deviations for example in the temperature fields. Finally, biogenic VOC emissions on a 10 km grid have been regridded again to the $0.5^{\circ} \times 0.5^{\circ}$ grid for use within CHIMERE.

In Fig. 1 we show total emissions of isoprene and the sum of terpenes for the year 2001, calculated with NatAir and D03 models. Data are displayed on the $0.5^{\circ} \times 0.5^{\circ}$ grid used for the CTM simulations. In the NatAir inventory elevated isoprene emissions (Fig. 1a) are found over the Iberian Peninsula (particularly Portugal and Southern

Spain), for France, Italy, North Africa, Balkans, Greece and Russia. Relatively low emissions are found for the UK, Central and Eastern Europe and Scandinavia. NatAir terpene emissions (Fig. 1b) are largest throughout the Iberian Peninsula, Southern France, Greece and parts of Italy. Relatively high terpene emissions are also found throughout Central and Eastern Europe and Scandinavia. Averaged over the whole domain, terpene emissions are nearly double of isoprene emissions.

Compared to emissions calculated with the D03 algorithm (Figs. 1c and d), NatAir isoprene and terpene emissions are generally increased over Iberian Peninsula and decreased over most of the other parts of Europe. In the NatAir inventory, Iberian Peninsula emerges as the largest European hot spot for isoprene and terpene emissions. Total isoprene emissions are roughly halved, while total terpene emissions are similar. NatAir emissions display finer structures in their spatial distribution, for example over France and the Balkans, as a result of the detailed species distributions used in calculations. Note that over Ukraine and Russia, emissions could not be calculated in D03 because of lack of input data. As said before, differences between both inventories can be due to a number of reasons, which could not be individually quantified in this study: a more detailed species distribution in the NATAIR inventory, updated emissions factors, taking into account the canopy effect, leading to lower emissions and taking into account a seasonality effect in the NATAIR inventory.

3. Results

In this section, we present the results of CHIMERE simulations with different biogenic emission inventories or without biogenic emissions. We first show the simulated impact of BVOC on average summer daily ozone maxima for a representative year (2001) using two different emission inventories (D03 and NatAir), in order to identify the most influenced regions in Europe. We then analyse the main factors driving the BVOC impact on ozone. We next analyse the inter-annual and seasonal variability of the impact. A subsection is devoted for comparing ground ozone observations with simulations, in order to check possible benefit in using the newly developed and more detailed inventory developed within NatAir, with respect to the D03 inventory.

3.1. Impact of emissions of biogenic volatile organic compounds on ozone

CHIMERE simulations with different biogenic emission cadastres as listed in Table 1 were carried out from 31 March to 31 October for years 1997, 2000, 2001 and 2003.

Fig. 2a shows average summer (JJA) 2001 daily ozone maxima in the first model layer for the CTRL run (no biogenic emissions). As will be shown in the following, elevated ozone values are simulated in the Mediterranean basin as a result of large anthropogenic precursor emissions in coastal areas, abundant solar radiation and small deposition rates. The Po Valley in Northern Italy appears by far as the most polluted region in Europe, with average daily ozone maxima up to 70 ppbv (54–66 ppbv in the rest of



Fig. 1. Biogenic VOC emissions used in this study for year 2001: (a, b) isoprene and sum of terpene emissions calculated within the NatAir project, (c, d) isoprene and sum of terpene emissions calculated with the algorithm described in Derognat et al. (2003), hereafter referred to as D03, based on Simpson et al. (1999). Annual totals for year 2001 averaged over the model domain are given in millions of tonnes (Tg). Totals for other simulation years are (from a to d): (1997) 2.9, 5.2, 5.5, 5.6; (2000) 3.0, 5.2, 5.9, 5.9; (2003) 3.5, 6.0, 6.7, 6.6 Tg.

Italy). The average ozone maximum over land reaches 47 ppbv (42 and 53 ppbv north and south of 47.5°N respectively), with a north-west to south-east gradient, in qualitative agreement with previous data from rural monitoring sites (Scheel et al., 1997).

BVOC emissions from the NatAir inventory (ALL2 simulation) increase daily ozone maxima over land by 2.5 ppbv on the average (respectively 1.3 and 4.0 ppbv north and south of 47.5°N, Fig. 2b). Change in ozone due to BVOCs peaks up to 20 ppbv at several locations in the Mediterranean area (Strait of Gibraltar, Aegean sea). At the country level, Portugal is the most impacted country. In

general, large changes are predicted throughout the Mediterranean Sea (average ~5 ppbv). It is interesting to notice that some of the most impacted areas are metropolitan regions of Porto (10–15 ppbv), Po Valley (5–10 ppbv), Marseille (5–8 ppbv) and Paris (4–6 ppbv). Also remarkably, in Spain, although BVOC emissions are large, ozone change is relatively small (2–4 ppbv), but larger along the populated coasts (4–10 ppbv) and Madrid (4–6 ppbv). These observations point out the importance of NO_x emissions, abundant in metropolitan areas and scarce in rural regions, as a necessary catalyst for efficient ozone production from BVOC oxidation. Note that over Northern

Table 1

List of ID and description of simulations presented in the manuscript

Simulation ID	Description
CTRL	No biogenic emissions
ALL1	CTRL+D03 isoprene
	and terpene emissions
ALL2	CTRL+NatAir isoprene
	and terpene emissions
ISO2	CTRL+NatAir isoprene emissions
TER2	CTRL+NatAir terpene emissions
CTRL-RED, ALL2-RED	Same as CTRL and ALL2, but with
	reduced chemical mechanism
CTRL-ISN, ALL2-ISN	Same as CTRL and ALL2, but with
	modified isoprene nitrate chemistry
CTRL-ANO40, ALL2-ANO40	Same as CTRL and ALL2, but with
	anthropogenic NO _x decreased by 40%
CTRL-BNO, ALL2-BNO	Same as CTRL and ALL2, but with D03
	biogenic NO emissions

D03 emissions are those described by Derognat et al. (2003). All simulations with anthropogenic emissions are from EMEP.

Scandinavia, ozone values are slightly reduced, due to ozonolysis of terpenes (see Fig. 4).

The differences in the predicted impact on ozone between the NatAir and D03 inventories (Figs. 2b and c) are largely consistent with the differences in emissions themselves. With respect to NatAir, D03 BVOC emissions have less impact on ozone in the Mediterranean and more in Northern Europe (average over land ozone change of 1.7 and 3.6 ppbv north and south of 47.5°N, respectively, 2.5 ppbv for the whole domain). For example, the effect of BVOC in Germany is 2–4 ppbv with NatAir and 3–5 ppbv with D03 emissions. In Portugal the change in ozone is 5–15 ppbv with NatAir and only 2–6 ppbv with D03 emissions.

In order to better understand the evolution of additional ozone due to BVOC over the whole Mediterranean area, we performed a particular experiment: BVOC emissions (NatAir in this case) are activated at a certain time (T0=00 UTC 29 June 2001) and the temporal behaviour of ozone compared to the CTRL run without biogenic emissions is analysed. In the morning of the first day (T=T0+11, Fig. 3a), the rising sun activates photochemistry and emitted BVOCs produce ozone near the sources, with maximum efficiency near populated and industrialized areas with large NO_x emission as previously noticed. Ozone is then distributed both over the continent and offshore, but at night it is consumed more rapidly over land (see e.g. Spain), because of more efficient dry deposition rate (*T*=T0+28, Fig. 3b). The following day, new BVOCs are oxidized, more ozone is produced and transported (T=T0+35, Fig. 3c) and then destroyed over land and accumulated over sea (T=T0+52, Fig. 3d). After 2-3 days the Mediterranean Sea is completely filled up with ozone produced from BVOCs (*T*=T0+59 and *T*=T0+76, Figs. 3e and f). Thus the interaction between precursor emissions, transport and land/sea differences in ozone dry deposition are responsible for the enhanced build-up of ozone in the Mediterranean basin with respect to the neighbouring continental rural areas.

Fig. 4 shows the separate contributions to ozone build-up from isoprene and the sum of terpene emissions for summer 2001 (simulations ISO2 and TER2 in Table 1). Over land, the average share of ozone production from BVOCs is about 60%



Fig. 2. Average effect of biogenic VOC emissions on summer 2001 surface ozone (daily maximum): (a) average daily ozone maximum simulated with CHIMERE in summer (JJA) 2001 without BVOC emissions (CTRL run, see Table 1), (b) ozone change including NatAir BVOC emissions (difference of ALL2-CTRL runs), and (c) ozone change including D03 BVOC emissions (ALL1-CTRL).



Fig. 3. Temporal evolution of the build-up of ozone produced by oxidation of BVOCs. Maps show hourly values of simulated ozone changes after the switch-on of BVOC emissions (*T*=T0) for three consecutive days at night (03Z) and morning (10Z).

from isoprene and 40% from terpenes, over sea it is 50% and 50% (Fig. 4). Ozone destruction in northern Europe is due to ozonolysis of terpenes. Note that the sum of individual contributions to ozone change is somewhat larger than that of combined isoprene and terpene emissions, indicating some non-linear effects in photochemistry.

The seasonal cycle of the BVOC impact on ozone is shown in Fig. 5 for April–September 2001. In April, when the growing season just begins, the prevailing effect is ozone consumption by terpene ozonolysis. In May, first BVOC emissions increase ozone in the Mediterranean region, then gradually also in other parts of Europe, being most effective in July and August. In September the BVOC effect on ozone levels in Europe is reduced to spring levels and in October it is negligible (not shown). This picture is consistent with the seasonal cycle of both BVOC emissions and photochemistry, both having a maximum during summer.

In Fig. 6, the inter-annual variability of the BVOC impact on ozone is displayed, for summers (JJA) in the years 1997, 2000, 2001 and 2003. The general pattern already described for 2001, with a negative gradient from south to north, is similar for all years. The year 1997 (average impact inland: 2.2 ppbv), a relatively hot year, is similar to 2001, while in 2000 (average impact: 2.0 ppbv), a relatively cold year, the lowest impact on surface ozone is observed, resulting mainly from reduced biogenic emissions and lower photochemical activity. The summer of 2003 (average impact: 2.8 ppbv) was characterized by several heat waves (Vautard et al., 2005 and references therein) and persisting high ozone levels. Such prolonged hot periods enhanced BVOC emissions, increasing their impact on ozone by 2–3 ppbv with respect to other years at some locations. In this year, in France the impact of BVOC on surface ozone is nearly doubled. In Portugal and the Po Valley, the area where BVOC produce more than 6 ppv additional ozone is strongly extended. The BVOC impact on ozone over the Mediterranean Sea is also significantly higher for the summer in 2003.

3.2. Comparison with ground observations

In order to investigate whether there is an improvement in simulations when introducing BVOC emissions, and in order to assess the performance of different BVOC emission inventories (NatAir or D03) on surface ozone, CHIMERE simulations are compared with observations at rural background monitoring sites (available from EMEP (http:// www.emep.int) and AirBase (http://air-climate.eionet. europa.eu/databases/airbase/) public portals). Data from 477 stations are used, mainly located in Germany (99 sites), France (70), Austria (54), Italy (23), Netherlands (23) and Spain (19). Results of the comparison between simulated and observed daily ozone maxima for 3 months of 2001 are given in Table 2 for three simulations (CTRL (no BVOC emissions), ALL1 (D03) and ALL2 (NatAir), see also Table 1).



Fig. 4. Individual contribution to ozone production from isoprene and the sum of terpenes (summer 2001): (a) ozone change due to isoprene (difference of ISO2-CTRL runs) and (b) ozone change due to the sum of terpenes (TER2-CTRL).

In the CTRL scenario, CHIMERE simulations show only a small bias in April and September, but underestimate ozone maxima in July. For all months, the underestimation is most pronounced over continental areas, with few exceptions for costal sites with a positive bias (e.g. UK, Po Valley and Bulgaria). This latter effect is likely due to the difficulties in simulating coastal breeze dynamics with the model resolution of 0.5°. The correlation with observations is much higher in July (~ 0.8) than in April or September (~ 0.6) . As we have previously shown, adding biogenic VOC emissions increases summer ozone values over the continent by ~ 2.5 ppbv on average, with local peak values of 15 ppbv at some places along the coasts (e.g. Portugal). As a consequence, the average negative bias comes closer to the measured values and is roughly reduced by a factor of two. In summer, the negative ozone bias at continental sites

is generally reduced, while the positive bias along the coasts is increased. The correlations are only slightly improved at a reduced RMSE. Model underestimation of ozone may partly be explained by the missing source of biogenic NO, that is not included in simulations, because it is considered too uncertain (see Section 4 for further discussion and sensitivity test, including these emissions). In April and September, changes in model performance when including BVOC emissions are small.

Regarding the impact of the two BVOC inventories on simulated surface ozone, differences with observed data are smaller than expected. It is likely that due to the coarse model resolution $(0.5 \times 0.5^{\circ})$ the advantage of the detailed BVOC source attribution by the NatAir inventory is veiled and higher model resolution of CHIMERE seems to be needed to assess the advantage of spatial and temporal high-resolution inventories in atmospheric chemistry modelling. It also has to be kept in mind that a modelled grid average ozone value is compared to a point measurement and that uncertainties resulting from other input variables (e.g. NO_x) as well as the chemical oxidation scheme contribute to the observed differences.

4. Uncertainties

In this section we estimate uncertainties related to our calculations. Evaluating the impact of biogenic VOCs on atmospheric chemistry is subject at least to three types of major uncertainties:

- (a) emission inventory,
- (b) modelling of chemical pathways,
- (c) ambient NO_x abundance.

Uncertainties related to the semi-empirical model used to estimate BVOC emissions are discussed in detail in the companion paper by Steinbrecher et al. (2008). Previously, Smiatek and Bogacki (2005) showed by Monte Carlo that biogenic emission uncertainties range from -70% to +70%for isoprene and from -60% to +140% for monoterpene emissions for forests in Poland. The differences between the two BVOC emission inventories used in our work (NatAir and D03, see Fig. 1) may be regarded as a proxy for the overall emission uncertainty. Indeed, regional differences in emissions range from -100% to 200% for isoprene and terpenes, which is a wider range than that deduced from the analysis reported but is still in uncertainty range of the emission inventories, including unknown systematic errors (e.g. Smiatek and Steinbrecher, 2006; Steinbrecher et al., 2008). The maximum difference in the calculated impact on ozone between the two inventories (Figs. 2b and c) is in the range of -3 to 8 ppbv. These values are observed in UK and Portugal, while over most of the continental area the calculated impact differs by less than ± 2 ppby.

Another source of uncertainty is how chemical degradation of BVOCs is treated in the model. Chemical mechanisms are in general condensed for reasons of computational efficiency on multi-year simulations, thus missing a detailed description of intermediate steps of VOC oxidation. The uncertainty related to this procedure is



Fig. 5. Seasonal cycle of BVOC impact monthly mean daily ozone maxima. Maps show ozone change using NatAir BVOC emissions (difference of ALL2-CTRL runs) from April to September in 2001.

addressed by performing a simulation scenario (summer 2001) with a reduced version of MELCHIOR (see Section 2.1), that contains about one half of the species and one third of reactions being used in standard applications with the CHIMERE model (Schmidt et al., 2001). In Fig. 7a we show that the calculated average ozone change due to NatAir BVOC emissions for summer 2001 decreases to 1.8 ppbv over land (0.9 and 3.0 ppbv north and south of 47.5°N, respectively). This is about –25% difference with the reference simulation (Section 3.1, Fig. 2b). The decreased impact is particularly evident in rural regions.

Recent modelling studies have pointed out that the impact of BVOC on ozone is particularly sensitive to the fate of isoprene nitrates (von Kuhlmann et al., 2004; Fiore et al., 2005; Horowitz et al., 2007). The reaction of hydroperoxy radicals formed from OH and O₂ addition to isoprene $[C_5H_8(OH)O_2]$ with NO leads to organic nitrate formation with an estimated yield between 4% and 15% (Horowitz et al., 2007 and references therein). This pathway strongly affects the NO_x budget, because organic nitrates can be removed by wet and dry deposition and because only part of NO_x (about 40%) is recycled back during further oxidation (Horowitz et al., 2007). Fiore et al. (2005) have shown that surface ozone concentrations over United States may vary up to 10 ppbv with a different assumption on isoprene nitrates. In the MELCHIOR mechanism, isoprene nitrates

are originally produced with a yield of 14%, they recycle back 50% of sequestered NO_x and they are not deposited. The sensitivity of our calculation to the fate of isoprene nitrates was tested by setting yield and deposition velocity to best estimates given by Horowitz et al. (2007), e.g. a 4% yield and deposition velocity equal to that of HNO₃. By doing so, more NO_x is consumed through deposition and less will be available for BVOC oxidation. The effect on calculated ozone change from NatAir BVOCs (Fig. 7b) is similar to that of using the reduced chemical mechanism. The impact of BVOCs decreases to 1.7 ppbv on average (0.9 and 2.8 ppbv north and south of 47.5°N, respectively) over land, which is about 30% lesser than with the reference simulation.

The analysis repeatedly shows how the impact of BVOC on ozone production is strictly tightened to the availability of NO_x. So far only anthropogenic NO_x sources (EMEP emissions) are included in the simulations presented with an uncertainty range of -40% to +40% (e.g. Beekmann and Derognat, 2003 and references therein). Performing a calculation with NO_x emissions reduced by 40% (Fig. 7c), we obtain an average impact of BVOC of 1.4 ppbv (0.6 and 2.3 ppbv north and south of 47.5°N, respectively), i.e. about 40% lesser than with the reference calculation. This almost linear response is explained considering that most of the continent is under a NO_x-limited regime (Tarasson et al., 2003).



Fig. 6. Inter-annual variability of BVOC impact on summer (JJA) daily ozone maximum. Maps show ozone change using NatAir BVOC emissions (difference of ALL2-CTRL runs) for the years 1997, 2000, 2001, and 2003.

A potentially important source of NO_x that we did not discuss so far is the biogenic NO emissions from soil. In CHIMERE this source is very simply parameterized (Derognat et al., 2003) and emissions are probably overestimated, and were not included in simulations described so far. The BVOC impact on surface ozone including biogenic NO emissions (Fig. 7d) is 3.0 ppbv (1.6 and 4.8 ppbv south and north of 47.5°N, respectively), that is +25% difference with reference. The difference is particularly pronounced in South-western France.

In summary, the analysis on the impact of different BVOC emission inventories on European ozone maxima simulated in a $0.5^{\circ} \times 0.5^{\circ}$ grid is not resulting in an overall positive or negative bias. The uncertainty related to

biogenic NO can potentially cancel out with the uncertainty related to the fate of isoprene nitrates produced photochemically. The overall uncertainty of BVOC on European surface ozone is estimated to be in the range of -50% to +50%. For particular regions like the Iberian Peninsula, south of France and the Po Valley the variability is much larger, amounting to a factor of two-three.

5. Conclusions and outlook

In the frame of the EU/FP6 Natural and Biogenic Emissions and Assessment of Impacts on Air Quality (NatAir project, http://natair.ier.uni-stuttgart.de/), we have investigated the impact of BVOC emissions on European ozone

Table 2

Statistics of ground level ozone maximum simulated with CHIMERE against observations at 477 rural background monitoring stations of EMEP and AirBase networks for the year 2001

	Sim. ID	April	July	September
RMSE (ppbv)	CTRL	7.6 (4.4–11.4)	12.6 (6.5-20.2)	7.9 (5.1–11.6)
	ALL1	7.4 (4.4–11.0)	10.6 (5.7–16.5)	7.8 (5.0–11.5)
	ALL2	7.5 (4.4–11.3)	10.8 (6.0–17.1)	7.8 (5.0–11.7)
Bias (ppbv)	CTRL	-1.4 (-8.3-5.0)	-7.6 (-17.1-0.7)	0.0 (-7.5-6.1)
	ALL1	-0.8 (-7.7-5.7)	-4.1 (-13.3-4.3)	1.4 (-5.9-7.1)
	ALL2	-1.2 (-8.2-5.4)	-4.2 (-13.4-3.9)	0.6 (-6.9-6.6)
Correlation	CTRL	0.58 (0.33-0.82)	0.78 (0.58-0.93)	0.52 (0.25-0.77)
	ALL1	0.61 (0.34-0.84)	0.80 (0.60-0.93)	0.55 (0.28-0.80)
	ALL2	0.59 (0.33-0.82)	0.79 (0.61–0.93)	0.53 (0.27–0.80)

Monthly root mean square error (RMSE), bias and correlation averaged over all stations are shown, with 10th and 90th percentiles in parentheses. Descriptions of simulation IDs are given in Table 1.



Fig. 7. Factors contributing to uncertainty in the calculation of BVOC impact on ozone. Ozone change from BVOC is calculated for summer 2001 for the following sensitivity simulations: (a) with reduced complexity of the chemical mechanism, (b) with modified chemistry of isoprene nitrates (less NO_x recycling, according to recent studies; Horowitz et al., 2007), (c) with anthropogenic NO_x emissions reduced by 40%, and (d) with added biogenic NO emissions.

levels. The CHIMERE chemistry-transport model has been run for 4 years (1997, 2000, 2001, 2003) during the vegetation-growing season (April–September) with BVOC emissions compiled within the NatAir project.

The NatAir BVOC inventory is based on a detailed plant type and chemical compound specific classification with corresponding updated emission factors, and includes a canopy and seasonality module (Steinbrecher et al., 2008). It represents the state of the art for describing European scale BVOC emissions. Compared to older emission inventories (Simpson et al., 1999) elevated isoprene and terpene emissions are estimated for the Iberian Peninsula, France, Italy and Greece. In Central, Eastern Europe and Scandinavia, terpene emissions usually dominate over isoprene. Isoprene emissions averaged over the domain are roughly halved, whereas average terpene emissions are of similar magnitude.

The effect of BVOCs emissions on European ozone levels is significant only in summer (IIA), when elevated BVOC emissions combine with fast photochemistry. We find that BVOC emissions increase summer ozone daily maxima over land by ~ 2.5 ppbv (or $\sim 5\%$) on average, Southern Europe being more affected than Northern Europe (1.3 and 4.0 ppbv north and south of 47.5°N, respectively). As supposed, summer of 2003 (characterized by heat waves) shows the largest impact of BVOC on surface ozone levels in Europe (about 25% more on average compared to the other years, but e.g. in France biogenically produced ozone doubled). Several factors have been determined, explaining the extent and spatial distribution of the impact of BVOC on ozone: (1) the importance of NO_x emissions, (2) the photochemical activity, (3) the transport, (4) ozone losses by dry deposition being more efficient over land. The uncertainty to daily surface ozone maxima resulting from BVOC oxidation on the basis of these factors has been evaluated by a first approach and a conservative uncertainty of \pm 50% is estimated for the modelling domain. Large BVOC impacts are estimated for the Mediterranean Sea (average \sim 5 ppbv) with some hot spots amounting to more than 20 ppby, e.g. bay of Gibraltar, east coast of Sicily and Greece). Other significantly impacted areas are metropolitan regions of Madrid (4-6 ppbv, 10%), Po Valley (5-10 ppbv, 15%), Marseille (5-8 ppbv, 15%) and Paris (4-6 ppbv, 12%). The percentage ozone changes resulting from BVOC oxidation calculated for these areas are comparable to previously reported values for particular events (see references in the introduction section).

Future work will be devoted to assess how this revised perspective of the role of biogenic emissions in southern and northern Europe can potentially affect air quality (ozone and particulate matter) control strategies with special focus on the Iberian Peninsula and the Mediterranean basin.

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