Atmospheric Environment 43 (2009) 1380–1391

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries

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ARTICLE INFO

Article history:
Received 26 November 2007
Received in revised form
16 September 2008
Accepted 26 September 2008

Keywords:
Isoprenoids
Sequiterpenes
oxyVOC
Inventory
BVOC
Emission modelling

ABSTRACT

Biogenic VOC emission estimates from the earth's surface are crucial input parameters in air quality models. Knowledge accumulated in the last years about BVOC source distributions and chemical compound species emission profiles in Europe as well as the demand of air quality modellers for a finer resolution in space and time of BVOC estimates have led to the set-up of new emission modelling systems. An updated fast BVOC emission modelling platform explicitly considering the seasonality of emission potentials and leaf temperature gradients in forest canopies by the semi-empirical emission module (seBVOC) will be proposed and used for estimating hourly values of chemical compound-specific emissions in Europe (33–68° north; 10° west to 40° east) in the years 1997, 2000, 2001, and 2003. Spatial resolution will be 10 km by 10 km. The database used contains latest land and forest distributions, updated foliar biomass densities, leaf area indices (LAI), and plant as well as chemical compound-specific emission potentials, if available. Meteorological input parameters for the respective years will be generated using the non-hydrostatic meteorological model MM5. Highest BVOC emissions occur in daytime hours around noon from the end of May to mid-August in the Mediterranean area and from the mid of June to the end of July in the boreal forests. Comparison of 3 BVOC model approaches will reveal that for July 2003, the European isoprene and monoterpene totals range from 1124 Gg to 1446 Gg and from 338 Gg to 1112 Gg, respectively. Small-scale deviations may be as high as $\pm 0.6\ \mathrm{Mg\,km^{-2}}$ for July 2003, reflecting the current uncertainty range for BVOC estimates. Key sources of errors in inventories are still insufficiently detailed land use data for some areas and lacking chemically speciated plant-specific emission potentials in particular in boreal, south-eastern, and northern African landscapes. The hourly emissions of isoprene, speciated terpenes, and oxyVOC have been made available by the NatAir database.

1. Introduction

Organic carbon in the atmosphere from biogenic as well as anthropogenic sources triggers the radical cycle in the atmosphere on global as well as on regional scales (e.g. Monks, 2005). Oxidation of volatile organic compounds (VOC) leads to changes in surface ozone as well as in the particle burden that will likely affect the people's health and plant productivity (e.g. Jenkin and Clemitshaw, 2000; EEA, 2007). Biogenic volatile organic compounds (BVOC) are emitted mainly from vegetation and temperature- and light-dependent in general (e.g. Guenther et al., 1995). The dominating biogenic compound emitted is isoprene (e.g. Simpson et al., 1999). In contrast to anthropogenic VOC (AVOC), BVOC are more reactive in the atmosphere (e.g. Atkinson, 2000) with a pronounced emission maximum in summer (e.g. Guenther et al., 1995; Smiatek and Steinbrecher, 2006). In high-pressure weather systems e.g. in June, July, and August with low wind speed, high insolation, combined with high NO_x levels and limited lateral exchange, surface ozone frequently exceeds air quality standards (e.g. WHO 100 $\mu g\,m^{-3}$; 8-hour average). In 2003 and again in 2006, for example, more than

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doi:10.1016/j.atmosenv.2008.09.072

50% of European urban population were exposed to air pollutant concentrations above certain limit values (EEA, 2007) despite the adopted precursor emission reduction legislation (e.g. VOC, NO_x; EU NEC directive; UNECE CLRTAP; Gothenburg protocol).

In consequence, air quality control measures in Europe do not appear to be as efficient as they should be. This observation might be partly explained by the still present or even enhanced emission of biogenic ozone precursors in particular at high temperatures and high solar radiation. It is evident that with reducing anthropogenic emissions of both VOC and NO_x, biogenic sources become increasingly important in atmospheric chemical processes. To estimate potential benefits of any emission reduction measure with respect to air quality, emissions have to be quantified in the most accurate way possible. For example, ozone creation in the atmosphere near large anthropogenic NO_x sources strongly depends on the prevailing specific VOC mix (e.g. Derwent et al., 2007; Theloke and Friedrich, 2007; Curci et al., 2009). Therefore, VOC totals often reported in emission inventories should be replaced by a chemical compound-specific list. Hence, much more efforts have to be undertaken to reduce uncertainties and close knowledge gaps related to chemical compound-specific source strengths in different emission categories, both anthropogenic and biogenic, and their spatial and temporal variability.

In contrast to man-made sources, biogenic ozone and particle precursors originate from diffuse and highly complex sources (e.g. forests, grassland) rather than line or point sources (e.g. roads, power plants). The biogenic emission of VOC, for example, is very small for grassland, but higher by about two orders of magnitude for an oak forest (Simpson et al., 1999). Consequently, sophisticated biogenic VOC emission inventories also require input data on detailed land use with a high spatial resolution. This was also underlined by Arneth et al. (2008) in a recent paper investigating global change effects on the isoprene emission of European forests.

This paper aims at investigating the variability in space and time of BVOC emission in an extended European area during cold and warm years using latest experimental data on the chemical compound-specific emission potentials of plants and European vegetation types and improved satellite data products (land use maps, leaf area indices) and modelling instruments (semi-empirical BVOC platform; Smiatek and Steinbrecher, 2006)). This modelling task is part of the project "Improving and applying methods for the calculation of natural and biogenic emissions and assessment of impacts on air quality" (NatAir; http://natair.ier.uni-stuttgart.de/).

2. Approach

2.1. Model description

The BVOC emission observed is calculated on the seBVOC model platform (Smiatek and Bogacki, 2005; Smiatek and Steinbrecher, 2006; Smiatek, 2007; Fig. 1). This emission model is based on algorithms presented by Guenther et al. (1993) and Guenther (1997) and discussed by e.g. Stewart et al. (2003), Zimmer et al. (2003), Hakola et al. (2006). In general, the emission E (in $\mu g\,m^{-2}\,h^{-1}$) of a BVOC species k from a plant species l can be quantified as:

$$E_{kl} = A_l D_l \varepsilon_{kl} \gamma \quad (1)$$

where A_l is the area covered by vegetation (m^2), D_l the foliar biomass (gm^{-2}), ε_{kl} an average emission factor μg (g-dry-weight)$^{-1}$ h^{-1}), and γ an environmental correction factor accounting for the temperature and light dependence of the emission. Emission factors are standardised emissions relating to 30 °C leaf temperature and 1000 $\mu mol\,m^{-2}\,s^{-1}$ photosynthetic active radiation (PAR).

BVOC emissions largely depend on temperature and solar radiation. The emission model distinguishes between synthesis emission (which depends on both light and temperature) and pool emission (which depends on temperature only). Isoprene emission is treated as synthesis emission. When modelling monoterpene emissions, three possibilities have to be considered: (1) synthesis emission only for e.g. *Quercus ilex* L., *Quercus coccifera* L., *Quercus suber* L., (2) synthesis and pool emissions for e.g. *Pinus pinea* L., *Picea abies* [L.] Karst., and (3) pool emission of e.g. *Betula pendula*, *Eucalyptus* sp. only (Steinbrecher et al., 1999; Shao et al., 2001; Niinemets et al., 2002; Hansen and Seufert, 2003; Staudt et al., 2004). Emissions of other VOC (oxyVOC, sesquiterpenes) are treated as pool emissions (Geron et al., 1994; Guenther et al., 1994; Koenig et al., 1995; Simpson et al., 1999; Stewart et al., 2003). It has to be noted that other VOC emissions are far less understood than isoprenoids, but there is some indication that emissions of some other VOC compounds, including a group of C_6 unsaturated hydrocarbons, are strongly influenced by external factors like wounding by microbes, insect pests or mechanical stress (Kesselmeier and Staudt, 1999; Guenther et al., 2000).

Total emission can therefore be described as:

$$E_{kl} = E_{kl\_P} + E_{kl\_S} \quad (2)$$

where E_{kl_P} results from pool emissions only and E_{kl_S} from the synthesis emission.

Total emission of the compound k in a NatAir grid cell is

$$Ek = \sum_{l=1}^{L} Ekl \quad (3)$$

where L is a total number of emitting plant species.

The seBVOC model was applied in a grid-based approach with a 10×10 km^2 grid in Lambert's azimuthal projection of the NatAir area based on the Inspire grid (Annoni et al., 2003) and defined e.g. by Theloke (2006) in a parallelised mode on a LINUX cluster computer.

2.2. Land use data

Land use distribution data on the plant species level are the data suited best for modelling biogenic VOC emissions. The NatAir domain forest data cover 116 different tree species on the area of the European Union (EU27) (Köble and Seufert, 2002). For the remaining area of the NatAir domain, land use data depicting general categories, such as coniferous, deciduous, and mixed forests, and other categories were applied. The data sets included: (1) CORINE, 2000 v5/05; (2) GLC northern Eurasia v4.0; (3) GLC Africa v5.0; GLC Europe v1.0, and GLC Global v1.1, 2003. From these data sets, a pan-European land cover mosaic has been constructed for the NatAir modelling domain (Köble, 2007). The final CLC2000–GLC2000 mosaic land use map contains 69 general land use categories. The forest and land use data were aggregated into the specified NatAir grid (10×10 km) of the Lambert's azimuthal map projection.

The general land use categories do not contain the same plant species in different parts of the modelling domain. The composition and, hence, BVOC emission of coniferous forest in Scandinavia differ from the coniferous forest composition in the Mediterranean. In order to reduce the possible bias, the emission potentials, foliar biomass as well as leaf area index (LAI) values were defined for 4 different climatic areas, taking into account potential vegetation cover (Bohn et al., 2000/2003). These areas include central Europe, northern Eurasia, Africa, and the Middle East.

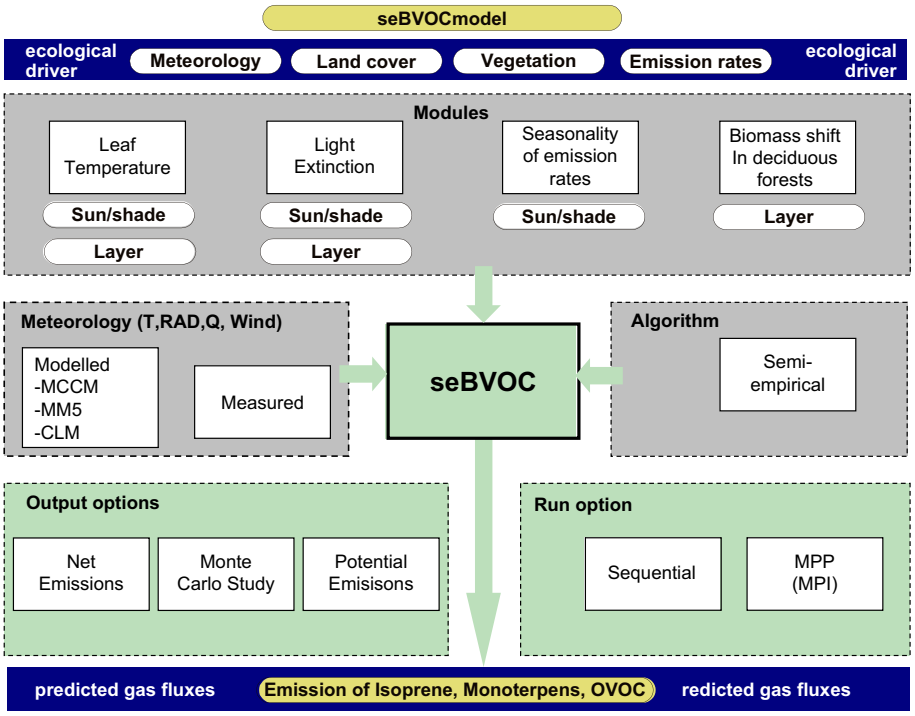

Fig. 1. The semi-empirical modelling platform seBVOC for estimating potential surface emissions of biogenic volatile organic compounds from terrestrial vegetation. MCCM: Mesoscale Climate Chemistry Model; MM5: Mesoscale Meteorological Model 5; CLM: Community Land Model; MPP: Massively Parallel Processing; MPI: Multiple Protocol Interface; OVOC: volatile organic compounds with heteroatoms of oxygen.

2.3. Emission factors and biometric parameters

Key input parameters of the seBVOC emission model are plant and chemical compound-specific emission potentials as well as leaf biomass. The values used in this modelling approach are listed in tables in the electronic supplement reflecting the current state of the art.

Existing emission potential databases (Kesselmeier and Staudt, 1999; Steinbrecher et al., 1999; Schaab et al., 2000; Owen et al., 2001; Mannschreck et al., 2002; Stewart et al., 2003; Parra et al., 2004; Wiedinmyer et al., 2004; Smiatek and Steinbrecher, 2006; Seco et al., 2007; MEGAN (Model of Emissions of Gases and Aerosols from Nature) http://acd.ucar.edu/~guenther/MEGAN/MEGAN.htm; Guenther et al., 2006) were used and updated according to recent experimental findings. Major updates of the emission potential were made for some fir species (*Abies borisii-regis*, Harrison et al., 2001; *Abies alba*, Moukhtar et al., 2005), Scots pine, Loblolly pine, Italian stone pine, Aleppo pine, Sitka spruce, and Norway spruce (*Pinus sylvestris*, Tarvainen et al., 2005; Hakola et al., 2006; *Pinus taeda*, Helmig et al., 2006; *P. pinea*, Noe et al., 2006; *Pinus halepensis*, Ormeño et al., 2007; *Picea sitchensis*, Hayward et al., 2004; *P. abies,* recalculated based on data from Steinbrecher, 1989; Schürmann, 1993; Rabong, 1995), European beech (*Fagus sylvatica*, Holzke et al., 2006; Moukhtar et al., 2005), Mediterranean oak (*Q. suber*, Pio et al., 2005; *Q. ilex*, Schaab et al., 2000; Owen et al., 2001), silver birch (*B. pendula*, Vuorinen et al., 2005), and *Eucalyptus* sp. (He et al., 2000) (Table 1; elec. suppl.).

The plant species-specific emission factors were used to calculate emission factors for regions without any detailed vegetation cover information being available. Average emission factors were estimated using the emission potential of the key plants in that area as a proxy (Table 2; elec. suppl.).

The study focussed on setting up a chemical compound-specific emission table. Chemistry transport models (CTMs), such as CHIMERE (see, Curci et al., 2009), require a detailed VOC speciation for air quality modelling. The following list of compounds has been compiled: isoprene, monoterpenes α-pinene, β-pinene, d-limonene, α-terpinene, γ-terpinene, camphene, Δ^3-carene, myrcene, *p*-cymene, trans-β-ocimene, cis-β-ocimene, α-phellandrene, β-phellandrene, sabinene, 1,8-cineol, α-thujene, linalool, sesquiterpene β-caryophyllen, and oxyVOC methanol, ethanol, formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid. Monoterpene emission was reduced to a single compound contribution in percent to the totals, for which the information was available (Table 3; elec. Suppl.). For plants without any experimentally determined chemical compound emission split, a default monoterpene split was assumed using the information available on other plants as a guidance (Table 4; elec. suppl.).

Information on sesquiterpene emission from plants is rare, but the number of experiments devoted to this issue is increasing, as suggested by the increasing number of plant species studied (see literature listed above for pines, birches, and oaks). Hence, sesquiterpenes were included in the emission factor database and represented separately by a default emission factor of β-caryophyllen.

Information on oxyVOC compounds emission from vegetation also is sparse, as shown in a recent review by Seco et al. (2007). This information was used to build up a default emission factor table that also included information from the MEGAN database (http://acd.ucar.edu/~guenther/MEGA/MEGAN.htm) with methanol as a key compound (60%) (Table 5; elec. suppl.).

Foliar biomass densities and LAI values vary significantly depending on forest age and natural growth conditions. Typical plant-specific values of foliar biomass and the leaf area index (LAI) were presented by Veldt (1989, 1991), Geron et al. (1994), Simpson et al. (1999), Lenz et al. (2002), and Breuer et al. (2003). For pines and Norway spruce, latitude-dependent leaf biomass densities were adopted according to the recommendations by Veldt (1989). Leaf biomass values for *F. sylvatica*, *Quercus petraea*, and pasture were updated based on recent literature (Dufrêne and Bréda, 1995; Harmoney et al., 1997; Wang et al., 2005; Leuschner et al., 2006)

(Table 7; elec. suppl.). In the case of lacking biomass or LAI values of plant species, default values were estimated using data from plants with similar leaf morphology as a proxy. In regions, where a more generalized vegetation information e.g. forest and shrub/grassland mosaic was available only, default biomass and LAI values were estimated on the basis of biometric data of the key plant distributions (Table 8; elec. suppl.).

2.4. Environmental correction factors

In seBVOC, light extinction within the canopy is taken into account by dividing the canopy into sunlit and shade fractions following the model presented by de Pury and Farquhar (1997). The corresponding leaf temperatures are determined by the canopy energy budget as shown by Dai et al. (2004), with the numerical solution being calculated by applying the iterative quasi-Newton–Raphson method.

A number of recent publications (Schnitzler et al., 1997; Staudt et al., 2000; Ciccioli et al., 2002, 2004; Schaab et al., 2003; Pio et al., 2005) indicate that BVOC emissions exhibit a seasonality of the emission rates. In the extended version, the environmental correction factor γ_s of the synthesis emission of isoprene and monoterpenes is therefore calculated as:

$$\gamma_s = C_L C_T C_S \tag{4}$$

For pool emission, the environmental correction factor γ_p is given as:

$$\gamma_p = K_T C_S \tag{5}$$

Guenther (1997) discusses in detail the calculation of the light C_L and temperature-dependent correction factors C_T and K_T. According to the results presented by Staudt et al. (2000), the seasonality correction factor C_S is calculated as follows:

$$C_S = 1 - \rho\left[1 - \exp\left(\frac{(D - D_0)}{\tau}\right)\right] \tag{6}$$

D is the month of the year, D_0 the month with the maximum emission rate (here, July), and τ is the length of the emission-active season in months. ρ is the ratio of the annual emission amplitude and the maximum emission rate $((\varepsilon_{max} - \varepsilon_{min})/\varepsilon_{max})$. For deciduous plants $\varepsilon_{min} = 0$ is assumed. For all other plant species or land use categories, a default value of $\rho = 0.8$ has been estimated, since the annual minimum of the emission factors is not known for most of the plant species.

In the case of deciduous vegetation types, τ is taken from the MODIS satellite data product LAI. For all other vegetation types, the default approach described below has been used.

The modelling domain has been divided into four geographical areas with the following parameter settings:

- Northern Europe (>65°): $D_0 = 7$ (July), $\tau = 12$ for evergreen and $\tau = 3$ for deciduous species
- Central Europe I (50–65°N): $D_0 = 7$, $\tau = 12$ for evergreen and $\tau = 5$ for deciduous species
- Central Europe II (40–50°N): $D_0 = 7$, $\tau = 12$ for evergreen and $\tau = 6$ for deciduous species
- Southern Europe (<40°N): $D_0 = 7$, $\tau = 12$ for evergreen and $\tau = 8$ for deciduous species

Evergreen plants comprise both coniferous and deciduous plants. In the present study, the start and duration of the vegetation period are estimated taking into account the seasonal behaviour of the leaf area index (LAI) derived from the MODIS data (Boston University). Doing this, the monthly LAI value is expressed as percentage of the maximum annual value. A significant increase/decrease of a monthly value clearly indicates the build up and senescence in deciduous canopies, as shown by Kellomäki et al. (2001).

2.5. Meteorological input parameters

The fifth generation Penn State University MM5 mesoscale NWP (numerical weather prediction) model (Dudhia, 1993; version 3.6) is used in order to produce meteorological fields of surface variables for input in the semi-empirical biogenic VOC emission model (seBVOC). The domain used covers Europe and adjunct areas with a horizontal resolution of 24 km. The grid uses a Lambert conformal projection and is centered at 18°E and 51°N. In order to cover the domain, 200×200 grid cells are established. The atmosphere is divided into 21 vertical layers from the surface to 100 hPa, with the first layer having a thickness of about 40 m, and about 10 levels below 1500 m above ground level (the typical boundary layer). Yearly simulations are made using 10 or 11 day periods. Every simulated day is initialised at 1800 TU on the day before in order to have a 6-hour spin-up period. In order to be close to reality, simulations are nudged to the European Centre for Medium-range Weather Forecast (ECMWF) 6-hourly reanalysis (ERA-40) for the years 1997, 2000, and 2001, and to operational analyses for 2003. Parameterisations and MM5 modifications for the simulations are similar to those used by Curci et al. (2009). Standard MM5 parameterisations are used, with modifications of the boundary layer and the microphysics schemes as in Chiriaco et al. (2006). The Noah-LSM land surface scheme is employed. The surface meteorological data have been re-sampled to 10×10 km^2 in order to fit the NatAir biogenic emission grid. Curci et al. (2009) compared the MM5 modelled data and observations, thus showing that the meteorological fields of the biogenic emissions are comparable. Application of an NWP instead of available reanalysis data was necessary to obtain an hourly data output with the higher spatial resolution desired. Hourly resolution of the BVOC inventory is required as input for chemical transport models (CTMs).

3. Results

The seBVOC model platform was used to estimate grid-based emissions (10 by 10 km) on hourly time scales for an extended area of Europe for the years 1997, 2000, 2001, 2003. The model output was used to derive several data sub-sets shown and discussed in the following chapters.

3.1. Annual, seasonal, and geographical variability

In Europe, BVOC emissions are dominated by forestal areas with isoprene being the most important compound emitted with a share of about one third of the emission of reactive compounds (Fig. 2). The other fraction is almost evenly distributed between the sums of monoterpenes and oxyVOC, such as alcohols, aldehydes, ketones, and acids. Sesquiterpenes contribute only 1–2% to the overall amount of compounds emitted. For other land use (all land use categories except for forests), BVOC emission is dominated by oxyVOC, making up about 50–60% of the total. BVOC emission in the extended European area was calculated for the years 1997, 2000, 2001, and 2003 representing fairly cold years as well as hot ones where the emission of 2003 may be taken as a proxy for 2050 BVOC emissions. The annual variation of BVOC emission for the main emitting months from May to September is about ±10% for both forestal areas and other land use.

BVOC emissions strongly depend on the annual cycle of temperature and light. In addition, vegetation and, thus, the emission-active surface change throughout the year. In

consequence, most of the emissions are observed in the leaf-on phase of the year, being highest in June, July, and August (Fig. 2). More than 95% of the emissions from European vegetation occur in the leaf-on phase with July as the month, where more than 40% of the yearly totals are emitted. Highest emissions were estimated for the relatively warm years 2001 and 2003 in July. It has to be noticed, however, that August BVOC emissions from forests in general are about 35% lower than in July and comparable to emissions in June.

In the course of the year, the VOC species profile emitted from European vegetation (Fig. 2) changes from hardly any isoprene emission in winter, early spring, and late autumn to summer emissions with almost identical fractions of isoprene, monoterpenes, and oxyVOC being released from forests. This indicates a partly high fraction of isoprene-emitting tree species (e.g. deciduous oaks) with a pronounced seasonal cycle being highly dependent on photosynthetic active radiation and temperature. For the rest of land use, compound contributions other than isoprene dominate, making up about 80% of the total BVOC emissions.

The geographical variation of isoprene and monoterpene emission in the modelling domain is shown in Fig. 3. In the high-emission season of the year, two hot spots in Europe are identified, one in the Mediterranean area and another one in Northern Europe. In these regions, mean emissions in the 10 km band at the corresponding latitude are as high as 4.5 kg km^{-2} day^{-1} for both compounds. Northern African landscapes are estimated to be isoprene emitters rather than monoterpene emitters. At latitudes between 48° and 55° north, mean emissions are small with less than about 1.5 kg km^{-2} day^{-1} for isoprene and 2.5 kg km^{-2} day^{-1} for the sum of monoterpenes. The peak emission season in the Mediterranean area lasts from mid-May to mid-August, whereas vegetation in boreal regions is active in producing VOC from mid-June to mid-July only (Fig. 3). Geographical areas with very low mean emissions (<0.5 kg km^{-2} day^{-1}) are characterised by a high fraction of water bodies in the 10 km latitudinal band analysed.

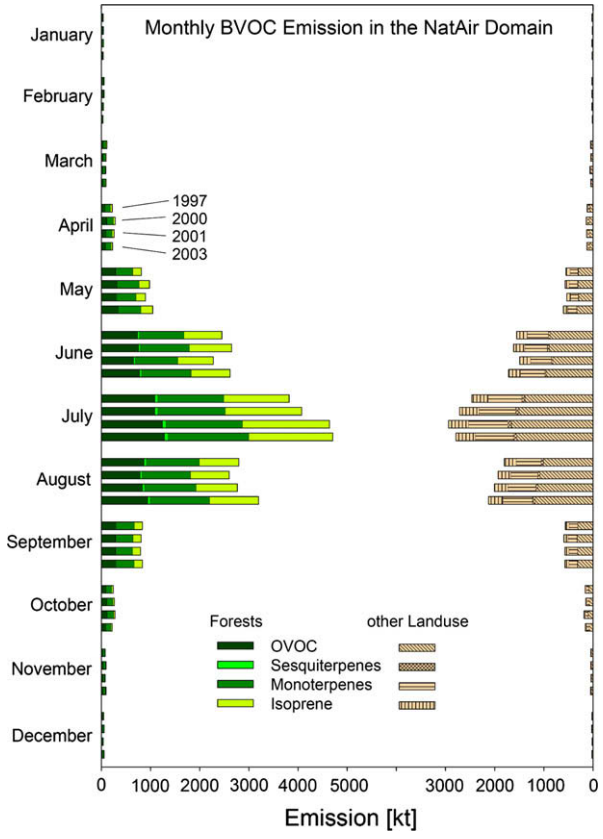

Fig. 2. Estimated monthly emissions of isoprene, mono-, sesquiterpenes, and OVOC (volatile organic compounds with heteroatoms of oxygen) in Europe, including neighbouring areas (domain area: 22.56 Tm^2) in the years 1997, 2000, 2001, and 2003. Other land use: all land use categories except for forests.

In July, highest emissions of up to 300 kg per km^2 per month for isoprene, monoterpenes, and oxyVOC are estimated for specific forest areas of Europe (Fig. 4). Total BVOC emissions may be as high as 1200 kg km^{-2} per month on the Iberian Peninsula, in Italy, Greece, Turkey, Finland, and Russia. Isoprene emissions are quite low in central Europe, Great Britain, Norway, Sweden, and Finland. European areas with a particularly high emission of monoterpenes are the Mediterranean countries and large parts of Russia, Finland, and Sweden. In these regions, high emissions of oxyVOC are observed as well.

3.2. Daily cycles of emission in Europe

BVOC emissions undergo a distinct diurnal variation as shown for the isoprenoids in Fig. 5. Isoprene experiences a pronounced midday maximum and hardly any emissions during the night. Monoterpene emissions still take place during the night due to the fact that emission from pools also occurs in the absence of light in contrast to emissions of freshly synthesised compounds, e.g. isoprene or monoteprene emissions from some evergreen oaks. Evergreen oaks are quite common in the Mediterranean Macchia and Garrigue, resulting in a quite high mean emission at the corresponding latitudes during daytime (around 0.9 kg km^{-2} h^{-1} in the 10 km band around 37° north) and about 90% less at night. The daily maximum emissions of isoprene and the sum of monoterpenes are comparable in this area. Again, an emission gap is observed in the northern part of central Europe, but emissions are increasing again further north. In these areas (>60°N; <65°N), mean isoprene emission increases again to around 0.6 kg km^{-2} h^{-1} during daytime and monoterpene emissions to about 0.3 kg km^{-2} h^{-1}. Nighttime monoterpene emissions in the northern part of Europe are comparable to those in the Mediterranean area (0.1 kg km^{-2} h^{-1}).

3.3. Country-specific emissions

Countries with highest emissions per ground area are Portugal, Cyprus, Spain, and Greece (Fig. 6; 5–8 t km^{-2} yr^{-1}), as the vegetation of these southern European countries is characterised by some of the highest emitters, e.g. oaks, *Eucalyptus*, aromatic plants of the Garrigue and Macchia (e.g. rosmary, thyme), and reed in river valleys. In these sometimes sparsely vegetated areas, the high emission potential combined with high solar radiation, high temperatures, and a long emission-active vegetation period result in the high emission densities observed. In countries further north and east, the vegetation consists of plant species with generally much lower emission potentials compared to Mediterranean plants (e.g. deciduous and coniferous trees, e.g. elder, elm, spruce, pine). These differences in the plant maximum-specific emission potential, together with a shorter emission-active period and lower maximum temperatures, results in BVOC emission densities that are smaller by a factor of three (2.8 tons per km^2 and year) in these parts of Europe.

4. Discussions and uncertainties

4.1. Emission modelling

The recently developed seBVOC modelling tool was used to estimate VOC emission from vegetation in European and neighbouring countries. The emission factors used were updated

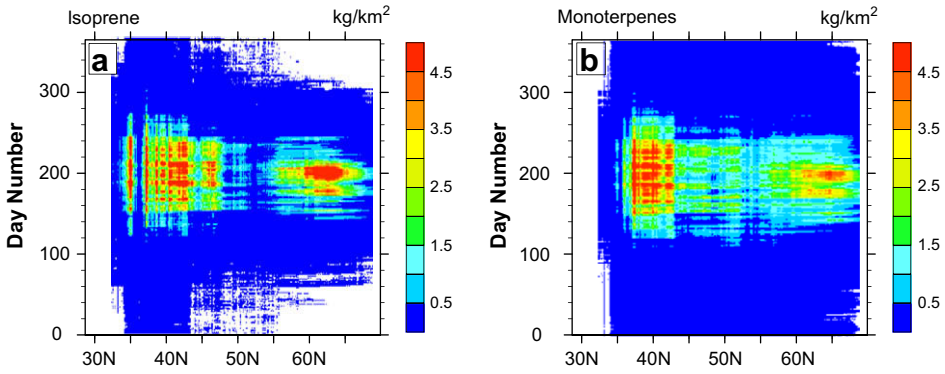

Fig. 3. Geographical and seasonal variations of isoprene and monoterpene emissions in Europe in the year 2000.

according to latest findings. In particular, the default emission factors for oxyVOC were increased by 25% based on some reports of high methanol emissions from plants (Seco et al., 2007). But still, large uncertainties exist in particular in the default values suggested for the sesquiterpene and oxyVOC emission factors as well as for emission factors assigned to general land use classes. No study is available in which all VOC species emitted from plants have been quantified on a compound-by-compound basis. In general, the emission studies focus on a specific set of compounds, e.g. mono- and sesquiterpenes from Scots pine (Hakola et al., 2006), methanol (Folkers et al., 2008). To overcome this problem, a default VOC emission species profile based on findings for the same family or genus is proposed. However, this approach still is rather rudimentary and reflects the need for more studies aiming at quantifying the chemical compound split emitted by the vegetation.

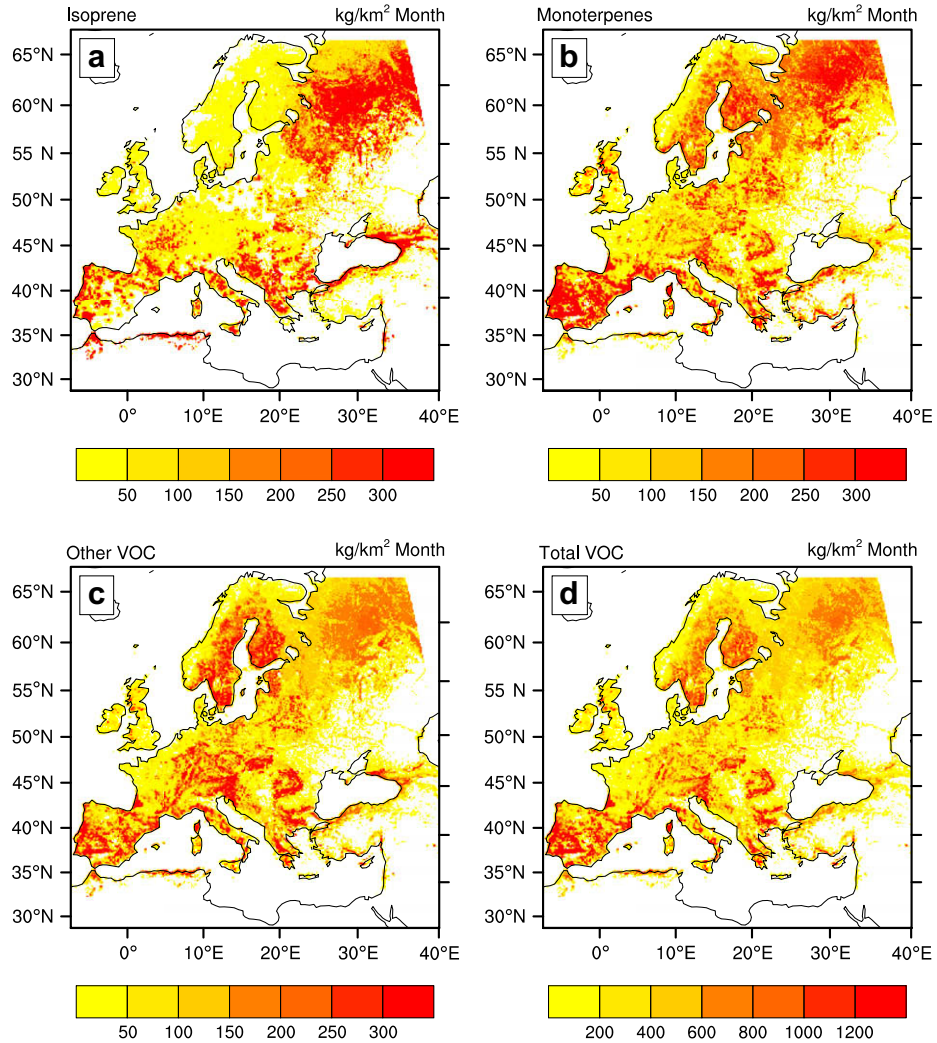

Fig. 4. Emissions of biogenic volatile organic compounds from terrestrial vegetation in Europe in July 2000.

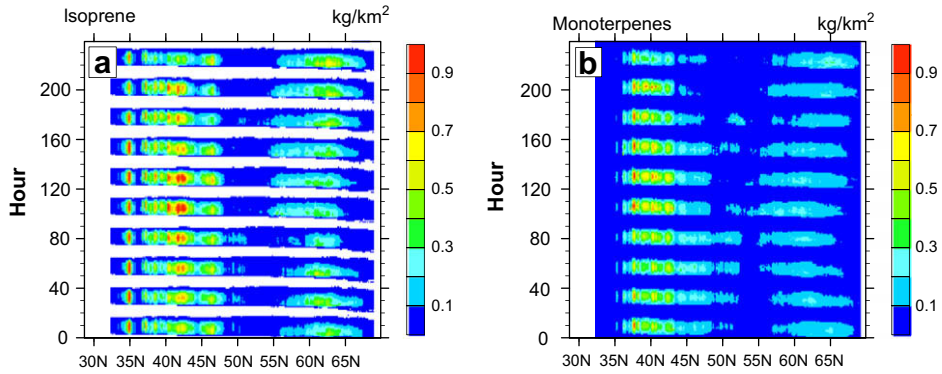

Fig. 5. Daily variations of isoprene and monoterpene emissions in Europe in the period from July 1st to July 10th 2000.

The modelling results presented do not include feedback effects resulting from the steadily increasing CO_2 concentration in the atmosphere and/or extended drought periods and other abiotic or biotic stresses possibly affecting VOC emission from vegetation (Plaza et al., 2005; Sharkey et al., 2007). No sound parameterisations of these effects are available due to the limited number of plants (mostly poplar and tobacco) studied. Moreover, ecosystem responses to these global change factors are not conclusive. As soon as well-established functional equations will have been developed, they will be included in an update of the model. Recently, it was shown by Arneth et al. (2008) how large the CO_2 effect on the European isoprene emission source strength from potential vegetation may be. For the period from 2081 to 2100, the inhibition of isoprene emission resulting from increasing CO_2 levels in the atmosphere could possibly cancel out the projected isoprene increase due to higher temperatures, increased leaf productivity, and leaf area. Intensive drought stress might play an important role in depressing summer emission around noon in hot countries, such as the Mediterranean (particularly Spain, Southern Italy, and Greece). If there is an extensive midday depression in photosynthesis as known for some plant species in the Mediterranean region, the temperature and light-dependent algorithms are no longer valid and main emission occurs in the early morning hours and afternoon only (Seufert and Ciccioli, unpublished results). Furthermore, this inventory does not consider any effects of biotic (such as insects, pests; e.g. Ibrahim et al., 2008) and other abiotic stresses (ozone, other photochemical pollutants; mechanical stresses; e.g. Beauchamp et al., 2005; Davison et al., 2008) that may reduce or increase the emission.

4.2. Land use

A major source of bias in balancing emission from vegetation using a modelling approach is incorrect land use classification. To reduce this bias, latest land use data sets with different levels of detailing were used. Whenever possible, plant species-specific land use information was used. However, general land use classes were available only in particular for countries in Eastern Europe, some parts of Southern Europe, and North Africa. In case of general land use classes, it is difficult to assign a "true" emission factor e.g. to broad leaf forests, as very low (alder, elm) as well as high VOC emitters (e.g. oak, poplar) exist in this category. To reduce the

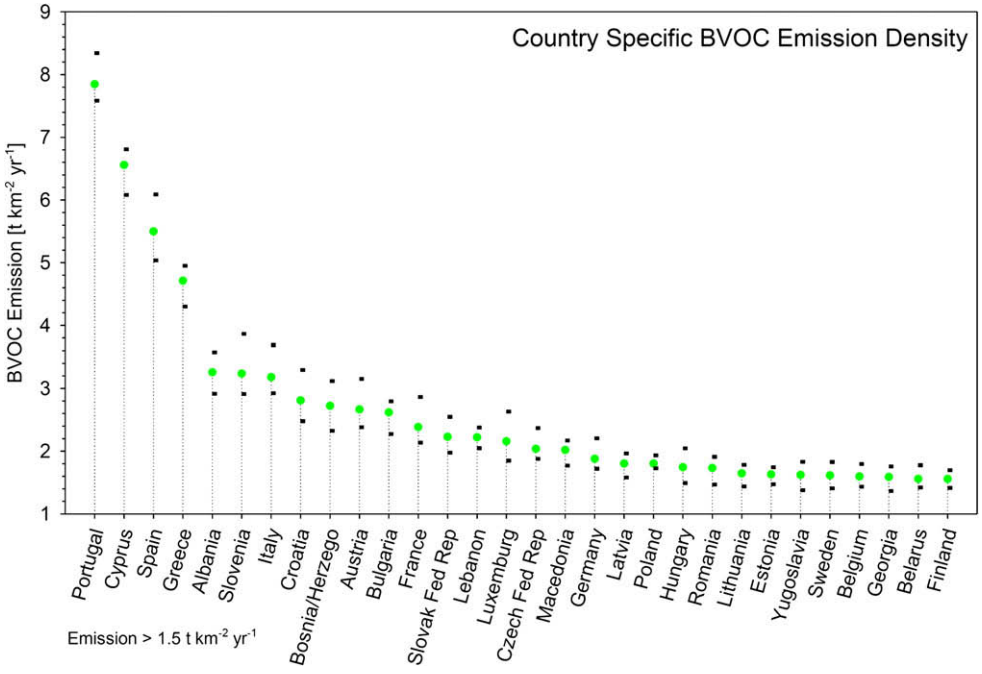

Fig. 6. Surface BVOC emission densities in selected European and neighbouring countries.

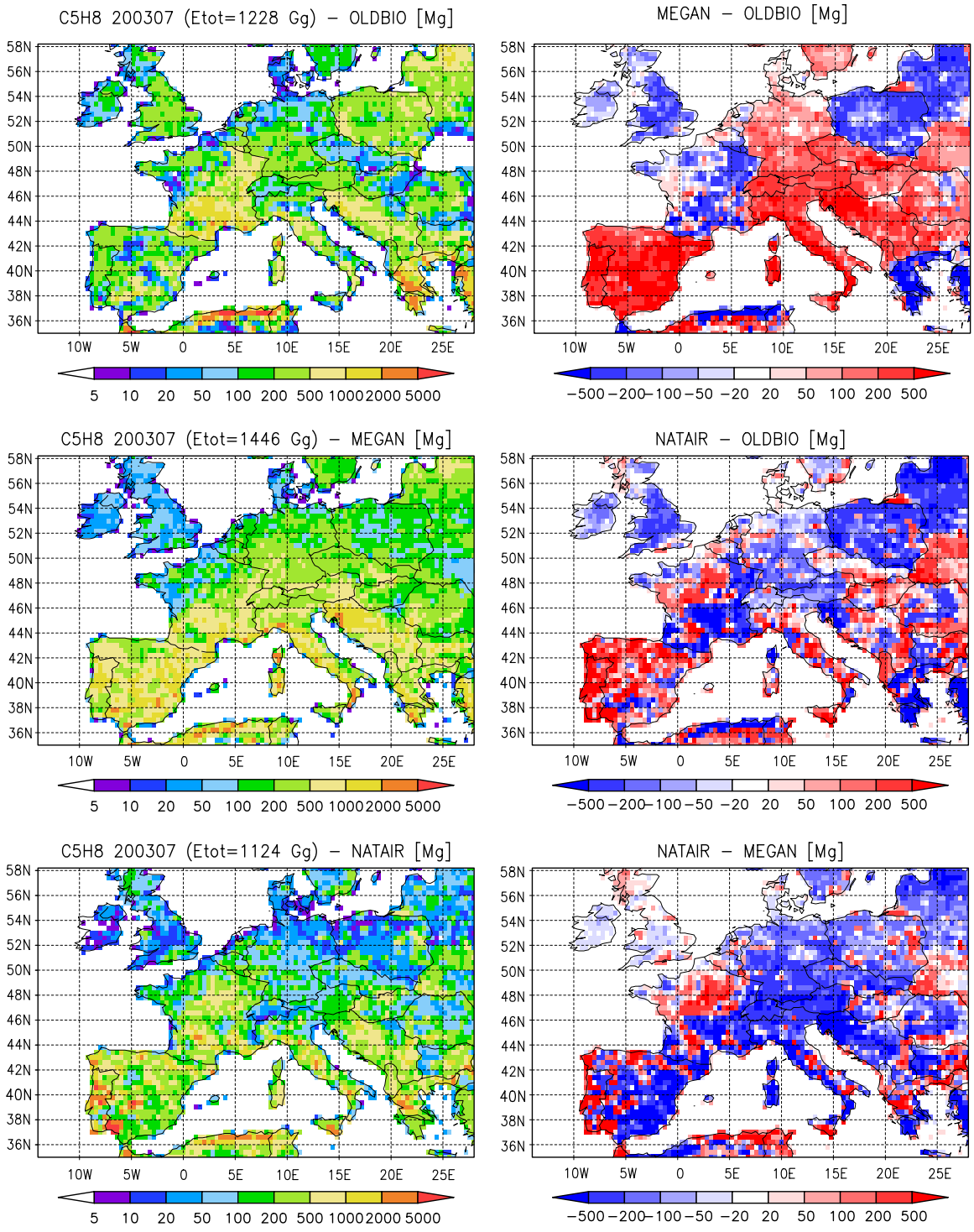

Fig. 7. Comparison of isoprene emissions in Europe for July 2003, which have been estimated by three different model approaches: Guenther et al. (2006) (MEGAN vs. Oct 2007), Simpson et al. (1999) (OLDBIO), and seBVOC (NATAIR). Grid size: 0.4° × 0.4°.

uncertainty in the emission factors estimated for general land use classes, the emission factors assigned to these classifications are weighted according to the dominant plant species.

In a case study for Belarus, the effect on emission source strength of both plant species-specific classification and general land use classification was investigated. The general land use classification resulted in a total emission smaller by about 30% (plant-specific: 277 kt; general land use: 208 kt for the year 2003) and a different VOC species profile emitted. The general land use classification resulted in a significant overestimation of isoprene by about a factor of five (general land use 73 kt vs. 15 kt plant-specific), but a significant underestimation of monoterpenes (general land use 80 kt vs. 143 kt plant-specific), sesquiterpenes (general land use 3 kt vs. 9 kt plant-specific), and oxyVOC (general land use 53 kt vs. 110 kt plant-specific). These large differences in the VOC species profiles emitted, which were obtained for two different land use data sets, will largely influence air chemistry in and above forests and, hence, regional air

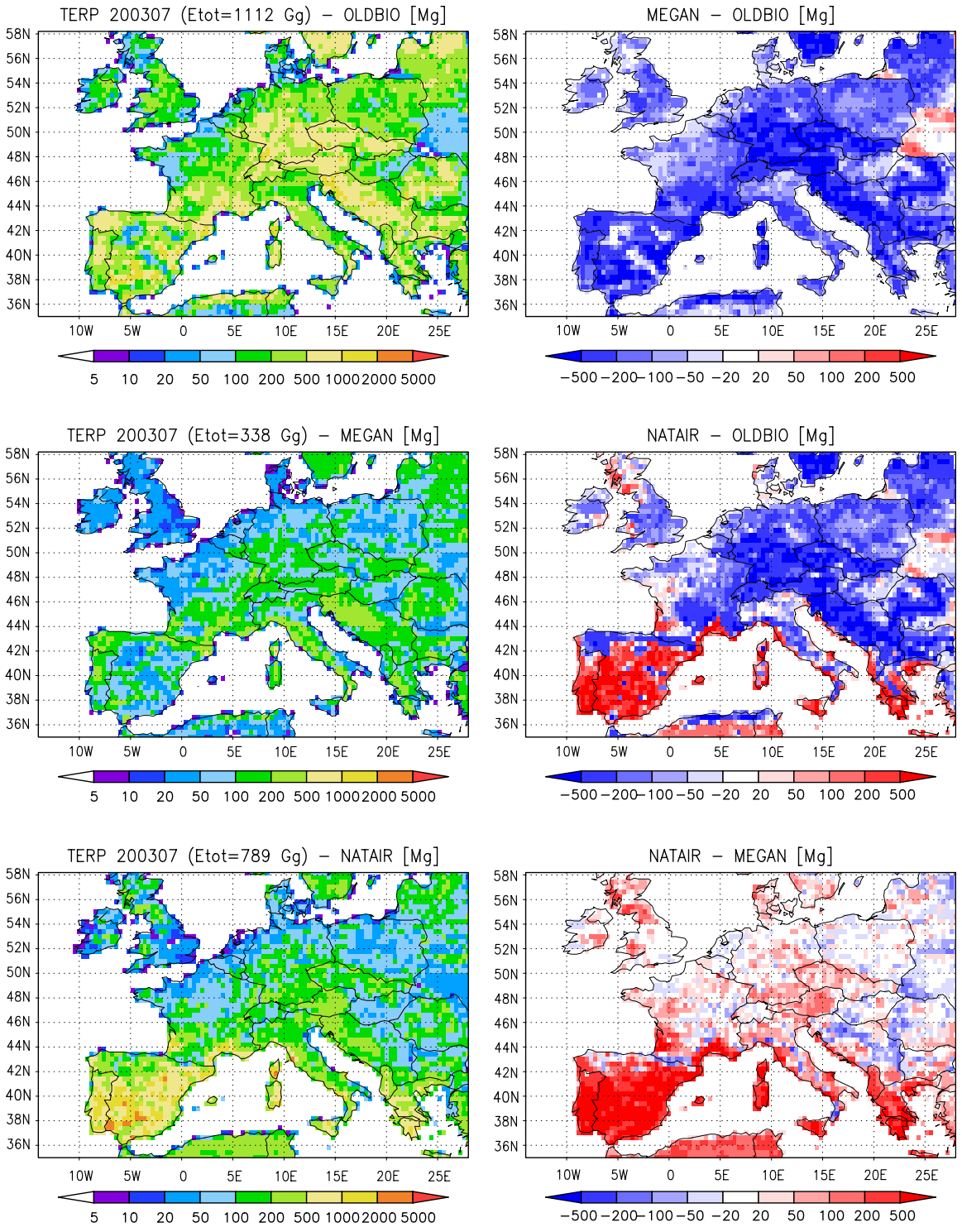

Fig. 8. Comparison of monoterpene emissions in Europe for July 2003, which have been estimated by three different model approaches: Guenther et al. (2006) (MEGAN vs. Oct 2007), Simpson et al. (1999), and seBVOC (NATAIR). Grid size: 0.4° × 0.4°.

quality modelling (Jenkin and Clemitshaw, 2000; Fuentes et al., 2007; Kourtchev et al., 2008). For this reason, more efforts will have to be taken to reach a high coverage of plant species-specific land use classifications for terrestrial vegetation and further reduce uncertainties and bias in chemical compound-specific BVOC emission inventories that are required by the modelling community to correctly assess surface ozone and particle production in the atmosphere.

4.3. Uncertainties

The new BVOC estimate presented here was compared to other inventories compiled using the same meteorological input data, but modelling approaches by (Simpson et al., 1999; OLDBIO) and (Guenther et al., 2006; MEGAN vs. Oct. 2007) (Figs. 7 and 8). For this comparison, isoprenoid emissions were assigned to a 0.4° × 0.4° grid in the modelling domain.

On the European scale, the different state-of-the-art inventory tools show some specific similarities, but also pronounced differences in isoprene and monoterpene emissions (Fig. 7). The total amount of isoprene emitted in the modelling domain in July 2003 ranges from 1124 Gg (NATAIR) to 1446 Gg (MEGAN), with a mean of 1266 ± 164.3 Gg (std) (Fig. 7, left panels). The variation resulting from the different approaches is remarkably low, with about 13% for the whole modelling domain. Regional differences, however, may be quite high and in the range of ± 500 Mg per grid cell in July 2003 (approx. 0.6 kg per km^2 per month) (Fig. 7, right panels). When comparing the variations on a geographical basis, the MEGAN approach generally resulted in significantly higher isoprene emissions in most parts of Europe. Compared to the OLDBIO approach, NATAIR estimates resulted in higher isoprene emissions in most parts of the Iberian Peninsula and Italy, but lower emissions in southern and eastern France, Poland, and the western part of Russia. It has to be noted that NATAIR and MEGAN emissions are quite similar in Great Britain and Eastern Europe, while the OLDBIO emission estimates match quite well with NATAIR emissions for Germany, Denmark, the Netherlands, Belgium, and southern Sweden.

A pronounced difference exists between the different model approaches for estimates of monoterpene totals in the modelling domain, which range from 338 Gg (MEGAN) to 1112 Gg (OLDBIO) (Fig. 8, left panels). The NATAIR and MEGAN approaches result in similar estimates for the northern and eastern parts of Europe, but significantly higher NATAIR emissions in the Mediterranean area and Portugal.

The differences observed between the MEGAN, OLDBIO, and NATAIR estimates (Fig. 8, right panels) may result from (a) different modelling approaches, (b) different land use data used, (c) different emission factors, and (d) different biomass densities or a combination of all factors mentioned. On a grid scale of ± 500 Mg per grid cell (approx. 0.6 Mg per km^2 per month), these differences in July 2003 currently represent the uncertainty in estimating BVOC emission in Europe. For some grid cells, this uncertainty is as large as the grid cell emission itself for both isoprene and the sum of monoterpenes.

5. Conclusions and outlook

Great progress has been achieved in understanding the processes governing VOC emission from vegetation as well as in improving land use classification. On the basis of latest findings, the BVOC emission estimate was updated for an extended area of Europe (EU member states, including countries from Eastern Europe, Central Asia, the Middle East, and Northern Africa). According to a comparison of three state-of-the-art BVOC modelling approaches, uncertainties in BVOC emission estimates sometimes are in the order of the grid cell emission itself. Having in mind that unknown feedback effects of interacting emission-controlling parameters (e.g. CO_2, soil drought, insect pest, air pollutants) may either lower or enhance BVOC emission, uncertainties of regional estimates may even be larger. As BVOC are largely involved in atmospheric chemistry and, thus, the cleansing capacity, it is of great importance to reduce the uncertainties of the emission estimates by:

(1) Further improving the land use database by including plant species-specific information with high spatial resolution.
(2) Studying the impact of additional emission-modulating factors identified, e.g. CO_2, ozone, drought, etc., on the source strength and VOC species profile emitted.
(3) Validating and further improving emission models by flux studies in key ecosystems that also include economic plants (e.g. plants used in bio-fuel production).

Meanwhile, the emission estimate presented may serve as an improved basis - despite the remaining uncertainties - for investigating the effect of biogenic emission on air quality in Europe, in a world of increasingly reduced anthropogenic VOC emissions due to the emission control directives adopted. In the future, BVOC emissions may become even more important in regional air chemistry of the atmosphere, as not only higher temperatures result in higher VOC emissions, but also an increased area of agro-forests with high VOC emitters, e.g. *Eucalyptus*, *Poplar* or palm trees planted for building CO_2 sinks and producing biomass for fuel production in the terrestrial biosphere.

Acknowledgements

Funding provided by the European communities for the NatAir project (contract number 513699) within the framework of FP6 is gratefully acknowledged. In addition, maintenance of the NatAir emission database by H. Pfeiffer from IER, University of Stuttgart, is acknowledged. We would also like to thank the two anonymous reviewers for their valuable comments on the manuscript.

Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2008.09.072.

References

Annoni, A., Bernard, L., Lillethun, A., Ihde, J., Gallego, J., Rives, M., Sommer, E., Poelman, H., Condé, S., Greaves, M., Uotila, P., Pinto, J.T., Torres, J.A., Lampinen, R., Kayadjanian, M., Schmidt-Seiwert, V., Meiner, A., Luzet, C., Wirthmann, A., 2003. JRC Action 2142 "European Spatial Data Infrastructure": 1st Workshop on European Reference Grids, Ispra, 27–29 October 2003 Draft summary 16.08.2004, Additional workshop material is available from: <http://gi-gis.jrc.it/ws/grid2003/index.html>.

Arneth, A., Schurgers, G., Hickler, T., Miller, P.A., 2008. Effects of species composition, land surface cover, CO_2 concentration and climate on isoprene emissions from European forests. Plant Biol. 10, 150–162.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. Atmos. Environ. 34, 2063–2101.

Bartalev, S.A., Belward, A.S., Erchov, D.V., Isaev, A.S., Bartholomé, E., Gond, V., Vogt, P., Achard, F., Zubkov, A.M., Mollicone, D., Yu Savin, I., Fritz, S., Repina, G., Hartley, A., 2003. GLC Northern Eurasia v4.0. The Land Cover Map for Northern Eurasia for the Year 2000. GLC2000 Database, European Commission Joint Research Centre. Available from: <http://www.gvm.jrc.it/glc2000>.

Beauchamp, J., Wisthaler, A., Hansel, A., Kleist, E., Miebach, M., Nienemets, U., Schurr, U., Wildt, J., 2005. Ozone induced emissions of biogenic VOC from tobacco: relationships between ozone uptake and emission of LOX products. Plant Cell Environ. 28, 1334–1343.

Bohn, U., Neuhäusl, R., unter Mitarbeit von/with contributions by Gollub, G., Hettwer, C., Neuhäuslová, Z., Raus, Th., Schlüter, H., Weber, H, 2000/2003. Karte der natürlichen Vegetation Europas. (Map of the Natural Vegetation of Europe). Landwirtschaftsverlag, Münster. Maßstab/Scale 1: 2,500,000.

Breuer, L., Eckhardt, K., Frede, H.-G., 2003. Plant parameter values for models in temperate climates. Ecol. Model. 167 (2–3), 237–293. doi:10.1016/S0304-3800(03)00274-6.

Chiriaco, M., Vautard, R., Chepfer, H., Haeffelin, M., Wanherdrick, Y., Morille, Y., Protat, A., Dudhia, J., 2006. The ability of MM5 to simulate ice clouds: systematic comparison between simulated and measured fluxes and lidar/radar profiles at SIRTA atmospheric observatory. Mon. Weather Rev. 134, 897–918.

Ciccioli, P., Baraldi, R., Mannozzi, M., Rapparini, F., Nardino, M., Miglietta, F., Brancaleoni, E., Frattoni, M., 2004. Emission and flux of terpenoids released from the terrestrial ecosystems present in the Pianosa. J. Mediterr. Ecol. 5, 41–51.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Brachetti, A., Marta, S., Loreto, F., Seufert, G., Vitello, M., Tirone, G., Manca, G., Valentini, R., 2002. Daily and seasonal variations of monoterpene emissions from an evergreen oak (*Quercus ilex* L.) forest of southern Europe. In: Hjorth, J., Raes, F., Angeletti, G. (Eds.), Proceedings of the 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants. Published on CD-ROM by The Institute of Environment and Sustainability, JRC of Ispra, DG Research, European Commission, Ispra, Italy Paper TO 4.

CORINE 2000 v5, 2005. The European topic centre on terrestrial environment: Corine land cover database 2000 – 100 m (Version 05/2005). Available from: <http://terrestrial.eionet.eu.int/CLC2000>.

Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R., Theloke, J., Friedrich, R., 2009. Modelling study of the impact of isoprene and terpene

biogenic emissions on European ozone levels. Atmos. Environ. 43, 1444–1455.
Dai, Y., Dickinson, R.E., Wang, Y.-P., 2004. A two-big-leaf model for canopy temperature, photosynthesis, and stomatal conductance. J. Clim. 17 (12), 2281–2299.
Davison, B., Brunner, A., Amman, C., Spirig, C., Jocher, M., Neftel, A., 2008. Cut-induced VOC emissions from agricultural grasslands. Plant Biol. 10, 76–85.
Derwent, R.G., Jenkin, M.E., Passant, N.R., Pilling, M.J., 2007. Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a Master Chemical Mechanism. Atmos. Environ. 41, 2570–2579.
Dudhia, J., 1993. A nonhydrostatic version of the Penn State/NCAR mesoscale model: validation tests and simulation of an Atlantic cyclone and cold front. Mon. Weather Rev. 121, 1493–1513.
Dufrêne, E., Bréda, N., 1995. Estimation of deciduous forest leaf area index using direct and indirect methods. Oecologia 104, 156–162.
EEA, 2007. Air pollution in Europe 1990–2004, EEA Report, 2, ISSN 1725-9177, pp. 80.
Folkers, A., Hüve, K., Amman, C., Dindorf, T., Kesselmeier, J., Kleist, E., Kuhn, U., Uerlings, R., Wildt, J., 2008. Methanol emissions from deciduous tree species: dependence on temperature and light intensity. Plant Biol. 10, 65–75.
Fuentes, J.D., Wang, D., Bowling, D.R., Potosnak, M., Monson, R.K., Goliff, W.S., Stockwell, W.R., 2007. Biogenic hydrocarbon chemistry within and above a mixed deciduous forest. J. Atmos. Chem. 56, 165–185.
Geron, Ch., Guenther, A., Pierce, Th, 1994. An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. J. Geophys. Res. 99D, 12773–12791.
GLC Global v1.1, 2003. The Global Land Cover Map for the Year 2000. GLC2000 Database, European Commission Joint Research Centre. Available from: <http://www.gvm.jrc.it/glc2000>.
Guenther, A., 1997. Seasonal and spatial variations in natural volatile organic compound emissions. Ecol. Appl. 7, 34–45.
Guenther, A., Ch., Geron, Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. Atmos. Environ. 34, 2205–2230.
Guenther, A., Hewitt, N.C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P.A., 1995. Global model of natural volatile organic compound emissions. J. Geophys. Res. 100, 8873–8892.
Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). Atmos. Chem. Phys. 6, 3181–3210.
Guenther, A., Zimmerman, P., Wildermuth, M., 1994. Natural volatile organic compound emission rate estimates for U.S. woodland landscapes. Atmos. Environ. 28, 1197–1210.
Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analysis. J. Geophys. Res. 98D, 12609–12617.
Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., Kulmala, M., 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. Biogeosciences 3, 93–101.
Hansen, U., Seufert, G., 2003. Temperature and light dependence of β-caryophyllene emission rates. J. Geophys. Res. 108 (D24), 4801.
Harmoney, K.R., Moore, K.J., George, J.R., Brummer, E.C., Russell, J.R., 1997. Determination of pasture biomass using four indirect methods. Agron. J. 89, 665–672.
Harrison, D., Hunter, M.C., Lewis, A.C., Seakins, P.W., Nunes, T.V., Pio, C.A., 2001. Isoprene and monoterpene emission from the coniferous species *Abies Borisii-regis* – implications for regional air chemistry in Greece. Atmos. Environ. 35, 4687–4698.
Hayward, S., Tani, A., Owen, S.M., Hewitt, C.N., 2004. Online analysis of volatile organic compound emissions from Sitka spruce (*Picea sitchensis*). Tree Physiol. 24, 721–728.
He, C., Murray, F., Lyons, T., 2000. Monoterpene and isoprene emissions from 15 eucalyptus species in Australia. Atmos. Environ. 34, 645–655.
Helmig, D., Ortega, J., Guenther, A., Herrick, J.D., Geron, Ch, 2006. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US. Atmos. Environ. 40, 4150–4157.
Holzke, C., Dindorf, T., Kesselmeier, J., Kuhn, U., Koppmann, R., 2006. Terpene emissions from European beech (*Fagus sylvatica* L.): pattern and emission behaviour over two vegetation periods. J. Atmos. Chem. doi:10.1007/s10874-006-9027-9.
Ibrahim, M.A., Stewart-Jones, A., Pulkkinen, J., Poppy, G.M., Holopainen, J.K., 2008. The influence of different nutrient levels on insect-induced plant volatiles, in Bt and conventional oilseed rape plants. Plant Biol. 10, 97–107.
Jenkin, M.E., Clemitshaw, K.C., 2000. Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. Atmos. Environ. 34, 2499–2527.
Kellomäki, S., Rouvinen, I., Peltoly, H., Strandman, H., 2001. Density of foliage mass and area in the boreal forest cover in Finland, with applications to the estimation of monoterpene and isoprene emissions. Atmos. Environ. 35, 1491–1503.
Kesselmeier, J., Staudt, M., 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. J. Atmos. Chem. 33, 23–88.
Köble, R., Seufert, G., 2002. Novel maps for forest tree species in Europe. In: Hjorth, J., Raes, F., Angeletti, G. (Eds.), Proceedings of the 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants. Published on CD-ROM by The Institute of Environment and Sustainability, JRC of Ispra, DG Research, European Commission, Ispra, Italy Paper TP 35.
Köble, R., 2007. Land use/cover map. In: NATAIR, Improving and applying methods for the calculation of natural and biogenic emissions and assessment of impacts to the air quality. European Commission – Sixth Framework Programme, Specific Targeted Research or Innovation Project. Proposal No.: 513699, Final activity report (Chapter 4.2).
Koenig, G., Brunda, M., Puxbaum, H., Hewitt, C.N., Duckham, S.C., Rudolph, J., 1995. Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species. Atmos. Environ. 29, 861–874.
Kourtchev, I., Ruuskanen, T.M., Keronen, P., Sogacheva, L., Dal Maso, M., Reissell, A., Chi, X., Vermeylen, R., Kulmula, M., Maenhaut, W., Claeys, M., 2008. Determination of isoprene and α-/β-pinene oxidation products in boreal forests aerosols from Hyytiälä, Finland: diel variations and possible link with particle formation events. Plant Biol. 10, 138–149.
Lenz, R., Köble, R., Seufert, G., 2002. Species-based mapping of biogenic emissions in Europe – case study Italy. In: Hjorth, J., Raes, F., Angeletti, G. (Eds.), Proceedings of the 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants. Published on CD-ROM by The Institute of Environment and Sustainability, JRC of Ispra, DG Research, European Commission, Ispra, Italy Paper TP 15.
Leuschner, Ch., Voß, S., Foetzki, A., Clases, Y., 2006. Variation in leaf area index and stand leaf mass of European beech across gradients of soil acidity and precipitation. Plant Ecol. 186, 247–258.
Mannschreck, K., Bächmann, K., Barnes, I., Becker, K.H., Heil, Th., Kurtenbach, R., Memmesheimer, M., Mohnen, V., Schmitz, Th., Steinbrecher, R., Obermeier, A., Poppe, D., Volz-Thomas, A., Zabel, F., 2002. A database for volatile organic compounds. J. Atmos. Chem. 42 (1), 281–286.
Mayaux, P., Bartholomé, E., Cabral, A., Cherlet, M., Defourny, P., Di Gregorio, A., Diallo, O., Massart, M., Nonguierma, A., Pekel, J.-F., Pretorius, C., Vancutsem, C., Vasconcelos, M., 2003. GLC Africa v5.0. The Land Cover Map for Africa in the Year 2000. GLC2000 Database, European Commission Joint Research Centre. Available from: <http://www.gvm.jrc.it/glc2000>.
Monks, P.S., 2005. Gas-phase radical chemistry in the troposphere. Chem. Soc. Rev. 34, 376–395.
Moukhtar, S., Bessagnet, B., Rouil, L., Simon, V., 2005. Monoterpene emissions from Beech (*Fagus sylvatica*) in a French forest and impact on secondary pollutants formation at regional scale. Atmos. Environ. 39, 3535–3547.
Niinemets, Ü., Hauff, K., Bertin, N., Tenhunen, J.D., Steinbrecher, R., Seufert, G., 2002. Monoterpene emissions in relation to foliar photosynthetic and structural variables in Mediterranean evergreen *Quercus* species. New Phytol. 153, 243–256.
Noe, S., Ciccioli, P., Brancaleoni, E., Loreto, F., Niinemets, U., 2006. Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics. Atmos. Environ. 40, 4649–4662.
Ormeño, E., Bousquet-Mélou, A., Mévy, J.-P., Geff, S., Robles, Ch., Bonin, G., Fernandez, C., 2007. Effect of intraspecific composition and substrate type on terpene emissions from some Mediterranean plant species. J. Chem. Ecol. 33, 277–286.
Owen, S.M., Boissard, Ch, Hewitt, C.N., 2001. Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale. Atmos. Environ. 35, 5393–5409.
Parra, R., Gasso, S., Baldasano, J.M., 2004. Estimating the biogenic emissions of non-methane volatile organic compounds from the North Western Mediterranean vegetation of Catalonia, Spain. Sci. Total Environ. 329, 241–259.
Pekel, J.-F., Vancutsem, N., Deofurney, P., Champeaux, J.-L., Gouveia, C., Lobo, A., Griguolo, S., Perdigao, A., Bartholomé, E., 2003. GLC Europe v1.0. The Land Cover Map for Europe in the Year 2000. GLC2000 Database, European Commission Joint Research Centre. Available from: <http://Www.Gvm.Jrc.It/Glc2000>.
Pio, C.A., Silva, P.A., Cerqueira, M.A., Nunes, T.V., 2005. Diurnal and seasonal emissions of volatile organic compounds from cork oak (*Quercus suber*) trees. Atmos. Environ. 39, 1817–1827.
Plaza, J., Núñez, L., Pujadas, M., Pérez-Pastor, R., Bermejo, V., García-Alonso, S., Elvira, S., 2005. Field monoterpene emission of Mediterranean oak (*Quercus ilex*) in the central Iberian Peninsula measured by enclosure and micrometeorological techniques: Observation of drought stress effect. J. Geophys. Res. 110 (D03303). doi:10.1029/2004JD005168.
de Pury, D.G.G., Farquhar, G.D., 1997. Simple scaling of photosynthesis from leaves to canopies without the errors of big-leaf models. Plant Cell Environ. 20, 537–557.
Rabong, R., 1995. Isoprene emission from spruce (*Picea abies* [L.] Karst.) of a mountain ecosystem and from oaks (*Quercus frainetto* Ten., *Q. petraea* (Matt.) Liebl., *Q. pubescens* Willd.) of a Mediterranean site, as well as control factors of isoprene emission and characteristics in the atmosphere. In: IFU Schriftenreihe, Bd. 35–95, ISBN 3-927548-78-2, Garmisch-Partenkirchen, pp. 300 (in German).
Schaab, G., Steinbrecher, R., Lacaze, B., 2003. Influence of seasonality, canopy light extinction and terrain on potential isoprenoid emission from a Mediterranean-type ecosystem in France. J. Geophys. Res. 108 (D13), 4392. doi:10.1029/2002JD002899.
Schaab, G., Steinbrecher, R., Lacaze, B., Lenz, R., 2000. Assessment of long-term vegetation changes on potential isoprenoid emission for a Mediterranean-type ecosystem in France. J. Geophys. Res. 105 (D23), 28863–28873.
Schnitzler, J.P., Lehning, A., Steinbrecher, R., 1997. Seasonal pattern of isoprene synthase activity in *Quercus robur* leaves and its significance for modeling isoprene emission rates. Bot. Acta 110, 240–243.

Schürmann, W., 1993. Needle Monoterpene Emission of *Picea abies* (L.) Karst. and Characteristics in the Atmosphere. PhD Thesis, Fakultät für Chemie, Biologie und Geowissenschaften Technische Universität München (in German).

Seco, R., Penuelas, J., Filella, I., 2007. Short-chain oxygenated VOCs: emission and uptake by plants and atmospheric sources, sinks, and concentrations. Atmos. Environ. 41, 2477–2499.

Shao, M., von Czapiewski, K., Heiden, A.C., Kobel, K., Komenda, M., Koppmann, R., Wildt, J., 2001. Volatile organic compound emissions from Scots pine: mechanisms and description by algorithms. J. Geophys. Res. 106 (D17), 20483–20492.

Sharkey, T.D., Wiberley, A.E., Donohue, A.R., 2007. Isoprene emission from plants: why and how. Ann. Bot., 1–14.

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, N., Janson, R., Khalil, M.A.K., Owen, S., Pierce, T., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrason, L., Öquist, M.G., 1999. Inventorying emissions from nature in Europe. J. Geophys. Res. 104, 8113–8152.

Smiatek, G., 2007. Distributed-memory parallelization of a semi-empirical biogenic volatile organic compounds emission model. Environ. Modell. Softw. doi:10.1016/j.envsoft.2007.07.009.

Smiatek, G., Bogacki, M., 2005. Uncertainty assessment of potential biogenic volatile organic compound emissions from forests with the Monte Carlo method: case study for an episode from 1 to 10 July 2000 in Poland. J. Geophys. Res. 110 (D23304). doi:10.1029/2004JD005685.

Smiatek, G., Steinbrecher, R., 2006. Temporal and spatial variation of forest VOC emissions in Germany in the decade 1994–2003. Atmos. Environ. 40, 166–177.

Staudt, M., Bertin, N., Frenzel, B., Seufert, G., 2000. Seasonal variation in amount and composition of monoterpenes emitted by young *Pinus Pinea* trees – implications for emission modelling. J. Atmos. Chem. 35, 77–99.

Staudt, M., Mir, C., Joffre, R., Rambal, S., Bonin, A., Landais, D., Lumaret, R., 2004. Isoprenoid emissions of *Quercus* spp. (*Q-suber* and *Q-ilex*) in mixed stands contrasting in interspecific genetic introgression. New Phytol. 163, 573–584.

Steinbrecher, R., 1989. Content and Emission of Monoterpenes of Tissues from *Picea abies* (L.) Karst. PhD Thesis, Fakultät für Chemie, Biologie und Geowissenschaften Technische Universität München (in German).

Steinbrecher, R., Hauff, K., Hakola, H., Rössler, J., 1999. A revised parameterisation for emission modelling of isoprenoids for boreal plants. In: Laurila, Th., Lindfors, V. (Eds.), Biogenic VOC Emission and Photochemistry in the Boreal Regions of Europe. European Communities 1999, ISBN 92-828-6990-3, pp. 29–43. EUR 18910 EN.

Stewart, E.H., Hewitt, C.N., Bunce, R.G.H., Steinbrecher, R., Smiatek, G., Schoenemeyer, T., 2003. A highly spatially and temporally resolved inventory for biogenic isoprene and monoterpene emissions – model description and application to Great Britain. J. Geophys. Res. 108. doi:10.1029/2002JD002694.

Tarvainen, V., Hakola, H., Hellèn, H., Bäck, J., Hari, P., Kulmala, M., 2005. Temperature and light dependence of the VOC emissions of Scots pine. Atmos. Chem. Phys. 5, 989–998.

Theloke, J., 2006. Overview of the NatAir project. In: Presentation at the 7th Task on Measurement and Modelling meeting in Helsinki Available from: <http://www.nilu.no/projects/ccc/tfmm/>.

Theloke, J., Friedrich, R., 2007. Compilation of a data base on the composition of anthropogenic VOC emissions for atmospheric modelling. Atmos. Environ. 41, 4148–4160.

Veldt, C., 1989. Leaf biomass Data for the Estimation of Biogenic VOC Emissions. MT-TNO report 89–306 Apeldoorn, 1989.

Veldt, C., 1991. The Use of Biogenic VOC Measurements in Emission Inventories. TNO-report no. 91–323 Apeldoorn, 1991.

Vuorinen, T., Nerg, A.-M., Vapaavuori, E., Holopainen, J.K., 2005. Emission of volatile organic compounds from two silver birch (*Betula pendula* Roth) clones grown under ambient and elevated CO_2 and different O_3 concentrations. Atmos. Environ. 39, 1185–1197.

Wang, Q., Tenhunen, J., Dinh, N., Reichstein, M., Otieno, D., Granier, A., Pilegarrd, K., 2005. Evaluation of seasonal variation of MODIS derived leaf area index at two European deciduous broadleaf forest sites. Remote Sens. Environ. 96, 475–484.

Wiedinmyer, Ch., Guenther, A., Harley, P., Hewitt, N.C., Geron, Ch., Artaxo, P., Steinbrecher, R., Rasmussen, R., 2004. Global organic emission from vegetation. In: Granier, C., Artaxo, P., Reeves, A. (Eds.), Emissions of Atmospheric Trace Compounds. Advances in Global Change Research, vol. 18. Kluwer Academic Publishers B.V., Dordrecht, The Netherlands, pp. 115–171.

Zimmer, W., Steinbrecher, R., Körner, C., Schnitzler, J.-P., 2003. The recently developed process-based model SIM-BIM realistically predicts isoprene emissions from adult *Quercus petraea* forest trees. Atmos. Environ. 37, 1665–1671.