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Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties

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Abstract

Large uncertainties exist in our knowledge of regional emissions of non-methane biogenic volatile organic compounds (BVOC). We address these uncertainties through a two-pronged approach by compiling a state of the art database of the emissions potentials for 80 European forest species, and by a model assessment and inter-comparison, both at the local and regional scale, under present and projected future climatic conditions. We coupled three contrasting isoprenoid models with the ecophysiological forest model GOTILWA+ to explore the interactive effects of climate, vegetation distribution, and productivity, on leaf and ecosystem isoprenoid emissions, and to consider model behaviour in present climate and under projected future climate change conditions. Hourly, daily and annual isoprene emissions as simulated by the models were evaluated against flux measurements. The validation highlighted a general model capacity to capture gross fluxes but inefficiencies in capturing short term variability. A regional inventory of isoprenoid emissions for European forests was created using each of the three modelling approaches. The models agreed on an average European emissions budget of 1.03 $TgC\,a^{-1}$ for isoprene and 0.97 $TgC\,a^{-1}$ for monoterpenes for the period 1960–1990, which was dominated by a few species with largest aerial coverage. Species contribution to total emissions depended both on species emission potential and geographical distribution. For projected future climate conditions, however, emissions budgets proved highly model dependent, illustrating the current uncertainty associated with isoprenoid emissions responses to potential future conditions.

These results suggest that current model estimates of isoprenoid emissions concur well, but future estimates are highly uncertain. We conclude that development of reliable models is highly urgent, but for the time being, future BVOC emission scenario estimates should consider results from an ensemble of available emission models.

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1 Introduction

Non-methane biogenic volatile organic compounds (BVOC), emitted by most plant species, is a heterogeneous compound class made up of a wide range of reactive volatile hydrocarbons. European forest species emit large amounts of BVOCs, in particular, volatile isoprenoids: isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) (Arneth et al., 2007; Guenther et al., 1995; Simpson et al., 1999).

For many BVOCs, the function for the emitting plants is not entirely clear (Owen and Peñuelas, 2005; Peñuelas and Llusia, 2004; Sharkey and Singsaas, 1995), although the emissions seem to play multiple roles in plant protection, in particular during episodes of high photosynthetic photon flux density (Sharkey and Singsaas, 1995), high temperatures (Copolovici et al., 2005; Peñuelas et al., 2005; Sharkey, 2005; Sharkey and Yeh, 2001), oxidative stress (Affek and Yakir, 2002; Loreto et al., 2001; Loreto and Velikova, 2001; Velikova and Loreto, 2005), and biotic stress (Miller et al., 2005; van Poecke and Dicke, 2004).

BVOCs play a significant role in atmospheric chemistry (e.g., Fuentes et al., 2000; Gelencser et al., 2007; Helming et al., 2006; Kanakidou et al., 2005; Szidat et al., 2006), in particular in the formation of secondary organic aerosols (Kanakidou et al., 2005) and tropospheric ozone at high light intensities and temperatures, and in the presence of NO_x (Fehsenfeld et al., 1992; Monson and Holland, 2001). Emissions from terrestrial ecosystems also cause a decrease in atmospheric hydroxyl radical (OH) concentrations and thereby result in an increase of the lifetime of methane in the troposphere (CH_4) (Poisson et al., 2000; Roelofs and Lelieveld, 2000). The emissions of BVOC have therefore far-reaching implications for air quality (e.g., Bell and Ellis, 2004), both globally and locally. The effects of biogenic emissions on methane lifetime and aerosols can further lead to important feedbacks between emissions and climate change (Kulmala et al., 2004; Peñuelas and Llusià, 2003).

Due to their importance in air chemistry and climatic processes, regional-scale emission inventories are needed to predict regional air quality as well as simulate future

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climatic conditions (e.g., Collins et al., 2004; Kulmala et al., 2004; Tunved et al., 2006). This requires application of emission models accurately describing the responses of emissions to variation in environmental drivers (Grote and Niinemets, 2008). Temperature and radiation have been found to be the main driving factors for the emission of both isoprene and monoterpenes in broad-leaved species (Dindorf et al., 2006; Hansen and Sharkey, 2001; Monson and Fall, 1989; Loreto and Sharkey, 1990), while only temperature has been suggested to control monoterpene emissions in some conifers (Tingey et al., 1980, but see Staudt et al., 1997). These key findings have driven the development of isoprene and monoterpene emission models from simple empirical models to more process based designs.

Early emission modelling methods took an empirical approach, linking emissions directly with climatic variables (Guenther et al., 1995). These have shown to have high predictive power in some, but not in all situations (e.g., Arneth et al., 2007; Bai et al., 2006; Geron et al., 2002; Harley et al, 2004; Otter et al., 2002, 2003; Wang et al., 2007). With an improved understanding of the biochemical reaction pathways for the formation of various plant volatiles, more mechanistic models have evolved (Bäck et al., 2005; Martin et al., 2000; Niinemets et al., 1999; Niinemets and Reichstein, 2003; Zimmer et al., 2000). In these process based models, responses of key enzymatic activities to environmental variables set the internal biochemical conditions, which finally determines the emission rates. These advanced models, however, still do not describe several key physiological observations (Monson et al., 2007), such as responses to elevated CO_2. These models also not always capture the variability in emission rates due to heat stress, and due to changes in stomatal closure as the result of drought or salinity stress. So far, few attempts have been made to compare the capacity of different emission models to simulate the environmental variability in emissions encountered in the field (Arneth et al., 2007).

Emission models are almost exclusively developed at the leaf level and are then scaled, through spatial and temporal scales, to the canopy, to the stand, and finally to the region level. This requires the coupling of an emission model with a process-

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based SVAT (soil-vegetation-atmosphere transfer) model. Such models describe leaf scale processes, set the micrometeorological canopy conditions which drive these processes, and describe the biomass and foliage distribution throughout the canopy (Baldocchi et al., 1999; Grote, 2006; Lamb et al., 1993; Lenz et al., 1997; Schaab et al., 2003). Such an approach also requires reliable information of emission potentials of each individual species.

The BVOC emission potential (E_S, the maximum emission rate under standard conditions) of terrestrial vegetation is one of the most important variables in modelling BVOC emissions (Arneth et al., 2008b; Grote and Niinemets, 2008). E_S strongly varies among species with values near zero to greater than 100 $\mu g\, g_{leaf}^{-1}\, h^{-1}$ (Kesselmeier and Staudt, 1999; Wiedinmyer et al., 2004). This high variability also exists between similar taxonomic entities (e.g., Owen et al., 2001) such that the emission potential of species of the same genera may be vastly different (Benjamin et al., 1996; Kesselmeier and Staudt, 1999). For instance, among *Quercus* species, some species are known to be strong isoprene emitters, some monoterpene emitters, and some species have emissions close to zero (Kesselmeier and Staudt, 1999). While extensive emission potential databases have been collated over recent years (Kesselmeier and Staudt, 1999; Wiedinmyer et al., 2004, http://bai.acd.ucar.edu/Data/BVOC/index.shtml; Nick Hewitt's database: http://www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf), these databases include all the estimates made so far without a critical revision. Even for a single species, a large variability exists in the emission factor estimates that is currently not understood. There is a general tendency of modelling studies to use average values of emission factors proposed by emission factor databases (Guenther et al., 2006; Parra et al., 2004; Simpson et al., 1995). However, as non-standardized methods have been used in the estimation of emission factors in the past, using averages of all estimates results in propagation of errors from study to study. Thus, a critical revision of the emission factors is pertinent to standardize the emission factor estimates as much as possible.

In this paper, we first embedded three different isoprenoid emission models into

a process based terrestrial biogeochemical model, thus providing a bottom up approach both to quantify the isoprene and monoterpenes emissions being released into the atmosphere under present day and potential future climate change. With these new tools we tested the possible variability due to differences in leaf level models. For this, isoprene emission flux measurements were used to compare diurnal and seasonal emission predictions at two forest sites with contrasting forest structure and species composition, one in the south of France and the other in Michigan, USA. We further revised the emission potentials for 80 dominant European forest species both occurring naturally and in forest plantations. In all cases, original studies were examined and a new consensus estimate was derived for each species. Using these basal emission potentials we derive an emission inventory for both isoprene and monoterpenes emissions from European forests under current climatic conditions using the three different modelling approaches. Finally, European forests were used as an example to analyse and compare large scale model performances under future climatic conditions.

2 Materials and methods

2.1 Leaf level emission algorithms

A recent model comparison study highlighted three isoprenoid emission models as possible candidates for regional or global applications (Arneth et al., 2007). The models take contrasting approaches to modelling emissions, each with different assumptions about the way environmental factors limit the emissions and with different levels of mechanistic detail. Where pertinent, modifications were made in order to ensure consistency between the models (as in Arneth et al., 2007). No direct CO_2 effect on the emissions was applied in the models.

2.1.1 Guenther et al. model

By far the most widely used models for simulation of natural isoprenoid emissions were developed by Guenther et al. (1991), and Guenther et al. (1993). Their approach was to describe the emission rates by using long-term basal emission factor for isoprene (E_I) and monoterpenes (E_M), and adjusting these basal emission potentials by two empirical factors, one describing the response to light intensity and the other to leaf temperature. The correlation between short term fluctuations, light intensity and leaf temperature is widely studied and much work has gone into validating the Guenther et al. model under different environmental conditions (Monson et al., 1994; Petron et al., 2001).

The emission factors used in the model are emission rates normalized to a leaf temperature (T) of 30°C and quantum flux density (Q) of 1000 µmol m^{-2} s^{-1} (sometimes for monoterpenes normalized only to temperature) (Guenther, 1991; Guenther et al., 1993, 1995, 1997). For light and temperature dependent isoprenoid emission, the following algorithm is used:

$$E = E_S C_L C_T \tag{1}$$

where E_S is E_I for isoprene and E_M for monoterpenes. C_L and C_T are the functions of quantum flux density and leaf temperature, respectively. C_L is a Michaelis-Menten type saturating function:

$$C_L = \frac{\alpha C_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}}, \tag{2}$$

where α and C_{L1} are empirical coefficients. C_T is described by an Arrhenius-type equation with an optimum that is commonly used to describe the temperature dependence

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of biological reactions:

$$C_T = \frac{E_{\text{opt}}.C_{T2}.\exp\left(\frac{C_{T1}.(T-T_{\text{opt}})}{RTT_{\text{opt}}}\right)}{C_{T2} - \left(C_{T1}.\left[1 - \exp\left(\frac{C_{T2}(T-T_{\text{opt}})}{RTT_{\text{opt}}}\right)\right]\right)} \quad (3)$$

where R, the gas constant, is 8.314 J K^{-1} mol^{-1}, and T_m is the temperature optimum, and C_{T1} the activation energy, and C_{T2} the deactivation energy. We used values of 95 000 J mol^{-1} for C_{T1} and 230 000 J mol^{-1} for C_{T2} from the original parameterization of Guenther et al. model. C_{L1}, α, E_{opt} and T_{opt} were determined following the algorithms developed by Guenther et al. (2006), which links these values to short term (24 h) and long term (10 days) fluctuations in temperatures and light intensity.

For some species, in particular conifers with extensive monoterpene pools with slow turnover compared with the rate of monoterpene synthesis, monoterpene emissions have been related directly to leaf temperature. In such cases, monoterpene emissions were calculated following Guenther et al. (1993) temperature based monoterpene model, as described by the following relation:

$$E = E_M \exp\left[\beta(T - T_s)\right] \quad (4)$$

where E_M is the basal emission rate at standard leaf temperature T_s (303.16 K) and β is an empirically determined coefficient. We used a value of 0.09 K^{-1} from the original parameterization of the model.

2.1.2 Niinemets et al. model

The Niinemets et al. model for isoprene and monoterpene emissions takes a process-based approach, linking the emission rates to the activity of the synthase enzyme S_S to predict the capacity of isoprenoid synthesis pathway and to foliar photosynthetic metabolism via the photosynthetic electron transport rate, J, to predict substrate availability for isoprenoid synthesis (Niinemets et al., 1999, 2002b). Here, the supply of

dimethylallyl pyrophosphate (DMAPP) and NADPH, as affected by the rate of photosynthetic electron transport and the competitive strength of the synthase enzyme for electrons, are considered as the main controlling factors for the rate of isoprenoid synthesis.

Emission rates are calculated through the fraction of total electron flow used for the isoprenoid synthesis, the rate of photosynthetic electron transport, and the cost of isoprenoid synthesis in terms of electrons. Thus, the emissions are linked to the photosynthetic activity of the leaf with the use of only one single leaf dependent parameter, ε, the fractional allocation of electron transport to synthase activity. Emission rates are given by the equation (Niinemets et al., 1999, 2002a):

$$E = \varepsilon J_T \frac{C_i - \Gamma^*}{\varsigma\,(4C_i + 8\Gamma^*) + 2\,(C_i - \Gamma^*)\,(\vartheta - 2\varsigma)} \tag{5}$$

where J_T is the total rate of photosynthetic electron transport, C_i is the internal CO_2 concentration, and Γ^* is the hypothetical CO_2 compensation point of photosynthesis that depends on photorespiration (Farquhar et al., 1980). ς is the carbon cost of specific isoprenoid (6 mol mol^{-1} for isoprene and 12 mol mol^{-1} for monoterpenes) and ϑ is the NADPH cost of specific isoprenoid (mol mol^{-1}). For isoprene, ϑ=14 mol mol^{-1}. For monoterpenes, ϑ is found as a weighted average of the costs of all terpene species emitted. In practice, $\vartheta \cong 28$ mol mol^{-1} as the contribution of oxygenated monoterpenes that may have lower electron cost or reduced monoterpenes that may have higher electron cost is generally small (Niinemets et al., 2002a, 2004). ε, the fractional allocation of electron transport to isoprenoid synthesis, is given by:

$$\varepsilon = F_d \frac{S_s}{J_{\max}} \tag{6}$$

where S_s is the specific activity of isoprenoid synthase (either isoprene or monoterpene synthase) in mol isoprenoid (g isoprenoid synthase)$^{-1}$ s^{-1} that depends on temperature according to an Arrhenius type equation that has a temperature optimum, and

J_{max} is the light saturated rate of total electron transport that scales with temperature in a similar manner (Niinemets and Tenhunen, 1997). F_d ($g\,m^{-2}$ mol electrons mol isopenoids^{-1}) is a scaling constant that depends on the basal emission rate, the isoprenoid synthase content ($g\,m^{-2}$) and also converts from isoprenoid units to electron transport units (mol isoprenoids mol electrons^{-1}) (Niinemets et al., 1999, 2002b). The isoprene and monoterpene models apply different values of ε.

2.1.3 Martin et al. model

Martin et al. (2000) developed a process based approach for isoprene emissions using the knowledge of the biochemical pathway of isoprene synthesis, thus providing a highly mechanistic model.

As the rate of isoprene emission will be governed by the rate of the slowest reaction in its biochemical pathway, the emissions can be calculated depending on which partial process is limiting under given environmental conditions. This model formulates the extent different processes in the biochemical pathway of isoprene synthase limit isoprene emission and represents the rate of emission as the minimum of three potentially rate limiting processes:

- The supply of carbon to isoprene synthase via pyruvate;
- The supply of ATP from phosphorylation;
- The temperature dependency of the isoprene synthase reaction rate.

Therefore, the isoprene emissions are given by:

$$E = L_d \min\{W_{isoco}, W_{isop}, V_{isoMax}\} \quad (7)$$

where L_d scales the hourly emissions to the basal emission rate. W_{isoco} is the pyruvate limited rate of synthase activity simulated by the flux of carbon through Rubisco:

$$W_{isoco} = \eta.\mathrm{FPYR}. \quad (8)$$

The parameter η describes the fraction of assimilated carbon lost as isoprene, which increases exponentially with temperature, and Fpyr is the rate of pyruvate formation from RUBP carboxylation.

W_{isop} is the rate of supply of ATP by phosphorylation, that depends on the carboxylation and photorespiration rates, the rate of dark respiration, and internal oxygen and carbon dioxide concentrations:

$$W_{isop} = \eta(V_c + 1.5V_{pr} - R_d)v, \quad (9)$$

where $v = [(O_i + V_c)/(C_i + V_{pr} + R_d)]$, V_c, V_{pr} and R_d are the rates of carboxylation, photorespiration and leaf dark respiration, respectively, C_i is the CO_2, and O_i the oxygen concentration in the leaf.

V_{isoMax} is the temperature dependence of the isoprene synthase enzyme as governed by an Arrhenius equation. The version applied here is a slight modification (following Arneth et al., 2007) of the original version used by Martin et al. (2000) in order to assure compatibility with the analogous expression in the model of Niinemets et al. The rate of isoprene synthesis is thus proposed to be highly dependent on the rate of supply of carbon in the form of phosphoglyceric acid (PGA) or pyruvate (from photosynthesis or photorespiration), the rate of phosphorylation to supply the ATP needed for the conversion of PGA/pyruvate to DMAPP and the amount and in vivo activity of the isoprene synthase enzyme (Lehning et al., 1999; Loreto and Sharkey, 1993; Monson et al., 1992), following the suggestion that Pyruvate is formed from Rubisco carboxylation about 1% of the time (Andrews and Kane, 1991).

Implicit in both the Niinemets et al. and Martin et al. model approaches for the simulation of isoprene emission on the basis of isoprene synthase kinetics (Fall and Wildermuth, 1998) is that DMAPP concentrations must change in response to changes in light availability at any given temperature, i.e. isoprenoid emission rates are substrate-controlled. DMAPP levels have been found to vary within and between days, and varied more in plants which emitted isoprene (Rosenstiel et al., 2002).

2.1.4 Modifying the leaf-level models to simulate long-term emission responses to environment

All three leaf-level models provide qualitatively similar responses of isoprenoid emissions to changes in temperature and light over short term (Arneth et al., 2007). However, emission rates also adjust to long term modifications in environmental drivers, implying that it is important to consider such effects as well to simulate long-term emission dynamics.

Phenology. Phenology is known to affect isoprenoid emissions and many studies have characterized how emissions respond to phenological events (e.g., Fuentes and Wang, 1999; Monson et al., 1994; Petron et al., 2001; Kuhn et al., 2004). Leaves begin to photosynthesize soon after budbreak, but isoprenoids are not emitted in substantial quantity for days to weeks after the onset of photosynthesis (e.g., Wiberley et al., 2005). This effect was incorporated into each of the emission models in the same simple manner as phenology affects seasonal photosynthesis, and also empirically implementing a time-lag between the onsets of photosynthesis and isoprenoid emissions. Seasonal photosynthetic capacity follows the Pelkonen and Hari (1980) approach, which introduces a factor K ranging from 0 to 1 depending of the stage of annual development. This factor multiplies the value of the maximum emission potential of fully-developed leaves used by each of the models. In the case of deciduous phenology (Smith et al., 2001) this leads to a decreasing isoprenoid emission capacity in senescing leaves before the leaves die (Arneth et al., 2007; Geron et al., 2000; Goldstein et al., 1998; Pressley et al., 2005).

Soil water availability effects. Isoprenoid emissions are effected by seasonal water stress, though the exact extent and mechanisms behind the emission responses to water stress are yet unclear (Grote and Niinemets, 2008). A strong reduction of emissions is observed in most cases after strong seasonal water stress (Llusia and Peñuelas, 1998; Pegoraro et al., 2004). In the model GOTILWA+, to which the emissions models are coupled, photosynthesis is reduced directly during water stress through a reduc-

tion in the rate of electron transport, and the maximum carboxylation capacity (Keenan et al., 2009). All three emissions models are indirectly influenced by the soil moisture dependence of stomatal conductance which influences the leaf temperature estimated by GOTILWA+. The Guenther et al. model also includes a direct effect of soil water stress. Emissions are reduced during water stress directly in parallel with photosynthesis, by applying the same function which reduces photosynthetic potential (Guenther et al., 2006; Keenan et al., 2009). Stress affects the Niinemets et al. model emissions indirectly, as the drought-dependent reductions in the rate of electron transport, J_T, lead to reduced substrate availability and thereby to reduced emissions. The Martin et al. model was modified in a similar manner as the Guenther et al. model, but here the water stress function was also applied to the supply of emission precursors.

2.2 Species-specific emission potentials

Calculated total emissions are highly dependent on the assigned emission potentials E_I and E_M (Eq. 1) that are directly applied in the Guenther et al. model, and determine the isoprenoid synthase activities in the Niinemets et al. and Martin et al. models. The emission potentials have recently been concluded to be one of the most important parameters for modelling regional emissions (Arneth et al., 2008b; Grote and Niinemets, 2008). In most large-scale modelling studies, the values initially specified by Guenther et al. (1995) are applied. Since then, much more information has become available and been integrated into previous estimates (Guenther et al., 2006). However, for most ecosystems and vegetation types measurements of BVOC emissions are still scarce or absent (Grote and Niinemets, 2008; Guenther et al., 2006). Due to the large variation within families, assigning general emission rates to plant functional types is often done by subjective judgment. It often occurs that very different emission potentials are assigned to a certain functional type or species in different modelling studies, leading to very different results (Arneth et al., 2008b for review). We address this problem through a thorough critical literature review to compile the state of the art knowledge of species-specific emission potentials for 80 species included in the GOTILWA+ forest

model (Table 1).

In this analysis, all previous known reports were reassessed with regards to measurement methods and derivation of standardized emission potentials. As there is considerable uncertainty in actual light and temperature environment in whole-tree and whole-branch enclosure studies that can seriously affect standardization of emission rates, we preferred estimates conducted with single leaf enclosures. As a variety of temperature responses have been used to convert the emission rates to standardized conditions of 30°C and 1000 µmol m^{-2} s^{-1}, whenever actual response curves were absent, we reconverted the data using the Guenther et al. (1993) original model. In all cases, units were homogenized (e.g., µg C g^{-1} hr^{-1} often used in North American studies vs. µg BVOC g^{-1} hr^{-1} often used in European studies). Errors due to the use of inappropriate values of leaf dry mass per unit area, M_A, in converting area based relations to mass basis (for instance converting total leaf area based estimates using projected area-based M_A values) were corrected.

Because of the lower sensitivity of analytical techniques in the past, and significant background level of isoprene and monoterpenes in the gas-exchange enclosures either due to isoprenoids in incoming ambient air, or adsorption/desorption processes in the cuvettes, there is considerable uncertainty in detecting minute emission rates with conventional techniques. Due to these uncertainties, emission rates less than 0.1 µg g^{-1} hr^{-1} were set to zero in the current compilation. Only the values corresponding to fully-developed leaves in non-stressed conditions were used whenever possible. For several species included in the GOTILWA+ model, reliable emission rates were not available. For these species, emission factors of taxonomically closest species were employed (Benjamin et al., 1996 for discussion).

For broad-leaved species not included in Table 1, we used the default values of 10 µg g^{-1} hr^{-1} for isoprene and 0.2 µg g^{-1} hr^{-1} as suggested by Solmon et al. (2004). For conifers not included in Table 1, the default values were 1 µg g^{-1} hr^{-1} for isoprene and 3 µg g^{-1} hr^{-1} for monoterpenes (Solmon et al., 2004).

In addition to the emission factors, for the simulation of monoterpene emissions, it

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is also important to know whether emissions are only temperature dependent or both light and temperature dependent. In several conifers, the emission may be both light and temperature dependent (Staudt et al., 1997; Shao et al., 2001) and information of the share or these two contrasting emission sources are provided in Table 1.

2.3 Scaling from the leaf to the landscape

The three emission models simulate isoprenoid emissions from any given leaf in dependence on climatic conditions. To scale from the leaf to the landscape, the emission models were coupled to the biogeochemical forest model, GOTILWA+. This model described leaf structural and chemical characteristics, and thus foliage physiological potentials. This model also described the microclimatic conditions and forest structure necessary to scale from the leaf to the canopy, and further to the region. Using forest inventories and regional databases of climate on a $10' \times 10'$ scale, simulations were run for each of the forest stands in EU15+2.

2.3.1 Scaling from the leaf to the stand: the GOTILWA+ model

Each emission model considered was coupled separately to the photosynthetic sub-model of the GOTILWA+ terrestrial biogeochemical model (Gracia et al., 1999; Keenan et al., 2008; http://www.creaf.uab.es/GOTILWA+). GOTILWA+ is a process-based forest model that has been developed to simulate carbon and water fluxes from forest ecosystems and to explore how the functioning of forests is influenced by climate, tree stand structure, management techniques and soil properties. Carbon and water fluxes of forests are simulated for different environmental conditions, for different tree species, and under changing environmental conditions that result from either climatic modifications or from alterations in management regime.

The GOTILWA+ model includes a two-leaf canopy photosynthetic model (Wang and Leuning, 1998; Dai et al., 2004). The photosynthesis sub-model treats the C_3 photosynthetic pathway. The canopy is divided into sunlit and shaded leaves, with the

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amount of intercepted diffuse and direct radiation depending on the time of the day, season, and the area of leaf exposed to the sun (Campbell, 1986, 1990). Foliage net assimilation rates are calculated using the Farquhar et al. (1980) photosynthesis model, with dependencies on intercepted quantum flux density, species-specific photosynthetic capacities, leaf temperature, and leaf intercellular CO_2 concentration (C_i). Stomatal conductance is calculated using the Leuning et al. model (Leuning et al., 1995) that is the advancement of the Ball et al. model (Ball et al., 1987). Water stress affects the photosynthesis-conductance coupling by directly reducing the photosynthetic potential through a non-linear relation to soil water content (Keenan et al., 2009). Canopy isoprene and monoterpene emission rates were calculated on an hourly basis as the sum of sunlit and shaded leaf fractions using their specific leaf temperature and incident radiation values.

The model treats monospecific stands which can be even- or uneven-aged. Individual trees in a stand are aggregated into 50 DBH (Diameter at Breast Height) classes and all calculations are performed for each class. Each tree cohort is represented by three carbon compartments, leaf, sapwood, and fine roots. Labile carbon is allocated to each, and maintenance respiration is calculated as a function of temperature. Fine litter fall (i.e. leaves and flowers), gross litter fall (i.e. bark, branches) and the mortality of fine roots add to the soil organic carbon content. The soil in GOTILWA+ is divided into two layers, an organic layer and a mineral layer, with a specific transfer rate of soil organic carbon between these two layers. Flux calculations are performed hourly, whereas slower processes such as growth and other state variables are calculated daily.

2.3.2 Scaling from the stand to the region

To supply the input data required by the model, an extensive database has been built within the framework of the European ATEAM (Advanced Terrestrial Ecosystem Analysis and Modelling) and ALARM (Assessing Large-scale Risks for biodiversity with tested Methods) projects, connecting diverse information sources at a European level

and adapting them to fit the same spatial resolution of 10′×10′. The database contains data related to forest species, forest area cover, forest structure, forest function (photosynthesis, respiration rates), soil hydrology, organic matter decomposition rates and management strategies (Schröter et al., 2005). Area explicit estimates of forest cover were made available which specify the eighty dominant forest species in Europe. Simulations were run with GOTILWA+ for each 10′×10′ scale forested pixel in Europe (EU15+2, pre-enlargement Europe, Norway and Switzerland). For parameterisation of the forest structural components in GOTILWA+, three forest functional types (temperate deciduous, temperate broadleaf evergreen, and temperate needle-leaf evergreen) were considered.

2.3.3 Scaling through time

Simulations were run with each emission model coupled to the GOTILWA+ model for a two hundred year period from 1900 to 2100. From 1900 to 2000, a reconstructed climatic data time series based on the CRU05 (1901–2000) monthly dataset (New et al., 1999) was used, with global atmospheric concentrations of CO_2 from 1901 to 2000 obtained from the Carbon Cycle Model Linkage Project (McGuire et al., 2001). The IPCC socioeconomic analysis (IPCC, 2001, 2007) resolved several possible standard scenarios for CO_2 emissions (A1, A2, B2, B1). Different global circulation models use these scenarios to generate future climatic projections. In this work we have applied the climatic projection for period 2001–2100 generated by the HadCM3 global circulation model using the A2 scenario as an indicator for the effect of possible future climate change on the BVOC emissions. This scenario uses an estimated increase in atmospheric CO_2 to 709 ppm by 2080. Using this scenario, HadCM3 predicts an increase in temperature of 2.8°C by 2080 for the area included in this study (in comparison to the average temperatures for the 1960–1990 period), and regional changes in precipitation.

2.4 Stand scale validation

Recent developments in methodologies such as eddy-covariance techniques provide high quality quantitative measurements of isoprenoid emissions (Ciccioli et al., 2003; Spirig et al., 2005). So far, few such measurements are available over forest ecosystems. Here, one relatively short-term series (26-days) of diurnal time-courses of isoprene emissions with a half-hour time-resolution (Arneth et al., 2007) and one long-term series of seasonal time-courses of isoprene fluxes with daily resolution (Pressley et al., 2005, 2006) are used to validate the implementation of the isoprene models at the canopy level. Three simulations were run at each site, one for each model coupled to the GOTILWA+ model, using stand and species parameters gathered from the literature (Arneth et al., 2007; Goldstein et al., 1998; Waring et al., 1998; Curtis et al., 2001; Pressely et al., 2006). Emissions factors were used from a previous modelling study at these sites (Arneth et al., 2007).

2.4.1 Site 1

We used measurements from two field campaigns at two Mediterranean *Quercus pubescens* stands in southern France (43° 39′ N, 6° E) conducted during 2000 and 2001. In these campaigns, isoprene fluxes were measured with the Eddy covariance technique for approximately two weeks in the summer of each year. The fast isoprene sensor (Hills and Zimmerman, 1990) was employed in these measurements, and half hour values were stored. These data have been used to examine the diurnal course of emissions predicted by each model. Average diurnal courses were constructed by taking the emission value for each hour of each day.

2.4.2 Site 2

To our knowledge, the only available long-term data set of forest eddy-covariance measurements of isoprene emissions is from the University of Michigan Biological Station

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(UMBS, 45° 33′ N, 84° 43′ W), (Pressley et al., 2005; http://www.biosci.ohio-state.edu/~pcurtis/UMBS~Flux). This site supports a mixed forest, dominated by *Populus grandidentata, P. tremuloides, Quercus rubra, Fagus grandifolia, Acer rubrum*, and *Pinus strobus* (Curtis et al., 2005; Pressley et al., 2005, 2006). Three years of eddy covariance measurements, from the growing seasons of 2000, 2001, and 2002, are available to test the model efficiency at capturing seasonal time-courses.

3 Results

3.1 Evaluating isoprene model emissions: diurnal time-courses

The data from the French site were used to test the capacity of the models to reproduce the diurnal time-courses of isoprene emissions. Each model compared well against the average diurnal time-course (Fig. 1). Guenther et al. model failed to reproduce the midday decline in emissions, and thus, overestimated the emissions at this site. Martin et al. model also overestimated the midday isoprene emission rate, but to a smaller extent. Niinemets et al. model accurately reproduced the early morning and late evening emissions, and also gave accurate estimates of the average diurnal midday emissions. When looking at the complete time series, no noticeable differences among model predictions can be discerned, except for the last five days of the measurement campaign in 2001. During this period, a large increase in the emissions was observed, which was accurately reproduced by both the Guenther et al. and the Martin et al. model. Niinemets et al. model, however, proved unresponsive during this period. This increase in the emissions was correlated with an increase in temperature during the last four days.

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3.2 Evaluating isoprene model emissions: seasonal time-courses

The seasonal time-course of isoprene emission was accurately simulated by each model (Fig. 2). The effect of phenological events during spring and autumn was well captured in 2000 and 2001. In 2002, missing data during spring complicated the comparison. The autumn reduction in isoprene emission was correctly predicted by the models. Day-today variability and summer maxima were reproduced with a lesser accuracy than the long-term phenological effects. The actual data exhibited a larger variability than the models in each year, in particular in 2000 and 2001. Both Guenther et al. and the Niinemets et al. model showed non-linear responses in their ability to simulate emissions, accurately capturing low level emissions ($\sim$<20 $mg_C\,m^{-2}\,d^{-1}$), but underestimating higher emissions. The Martin et al. model showed a more linear response, with a slight tendency to underestimate emissions in all cases.

3.3 Current emissions from European forests

Total simulated isoprene emission from pre-enlargement European Union with Norway and Switzerland (EU15+2) was 1.03 $TgC\,a^{-1}$ for the period between 1960 and 1990. A broad range of canopy emission capacities was observed for the species considered (Fig. 3), with order of magnitude differences per unit ground area. However, when considered together with species aerial coverage and climatic distribution, the strongest emitters were not necessarily the largest contributors to the European emission budget. The Europe-wide isoprene emission was dominated by a few species. *Quercus robur* was by far the highest contributor, with 32% of total Europe-wide emission. *Quercus pubescens* and *Quercus petraea* contributed 18% and 16%. *Eucalyptus* species, *Quercus frainetto*, and *Quercus pyrenaica* each contributed around 6% to total emissions. Six species contributed between 1 and 2% (*Quercus faginea*, *Quercus rubra*, *Populus* spp., *Robinia pseudacacia*, *Picea abies)*, with the remaining species contributing less than 1% of the total European emission budget.

Monoterpene emissions showed a similar pattern, with a very broad range of species

emissions per unit stand area, but with only a few species dominating the total budget of emissions from European forests when both emission potentials and geographical distribution were taken into account. Total simulated emissions amounted to 0.93 TgC a^{-1}. Of this total, 24% was emitted by forests dominated by *Quercus ilex*, 21.5% by *Pinus sylvestris*, 16% by *Fagus sylvatica*, 11% by *Picea abies* and 7% by *Quercus suber*. Seven further forest species (Fig. 4) contributed between 1 and 2% to total emissions, with the remaining forest species contributing less than 1%.

Emissions showed a strong regional pattern, being influenced by the distribution of the species across Europe, and regional weather patterns. For isoprene emission, France showed the highest emissions for the period 1960–1990 (Fig. 5), followed by the north-western area of the Iberian Peninsula. The Mediterranean zone, although it is subject to higher temperatures, and radiation, showed lower emissions than central mainland Europe due to lower plant coverage and leaf area index as well as due to suppression of emissions during extensive summer drought periods.

Simulated monoterpene emissions were lower than those of isoprene, with lower interspecific emission rate variability. The emissions of monoterpenes also showed a more uniform spatial distribution. The highest emissions were predicted for the southern Iberian Peninsula, and areas of the Mediterranean zone (Fig. 6).

3.4 Model comparisons for the period 1960–1990

The period 1960–1990 is often used as a baseline for comparing regional models in the past and the future (Schröter et al., 2005). For isoprene, no significant difference was observed between the emission model predictions for this period. The three isoprene models agreed on the total emission budget, and gave similar responses to light and temperature ranges across Europe. For monoterpenes, the Guenther et al. model gave slightly higher (4.6%) emissions than the Niinemets et al. model for the simulated period, perhaps due to a slightly stronger temperature response (Arneth et al., 2007).

3.5 Projected future European emissions

Although the choice of the model had little effect on the estimated budget of isoprenoids during the period 1960–1990, projected future emission estimates were greatly affected by the choice of the emission model. In the case of isoprene, the models showed up to a two-fold difference in predicted emission rates by 2100 (Fig. 7). Differences were not fully evident until about 2050, when large disparities began to appear between the models. All models agreed on a general strong increasing trend in both isoprene and monoterpene emissions, though the dynamics of this trend differed between models. For isoprene emission, Martin et al. model showed the strongest response with average per pixel emission of 4400 $mg_C\,m^{-2}\,a^{-1}$ from European forests. This gave a total European budget of 2.36 $TgC\,a^{-1}$ for the period 2080–2100, i.e. more than double the average emission predicted for the period 1960–1990 with the same model. Guenther et al. model gave slightly higher emissions than the other models for the early 21st century, but did not respond as strongly as Martin et al. model under conditions of more severe climate change (3720 $mg_C\,m^{-2}\,a^{-1}$ for 2080–2100). Total European isoprene emission simulated with the Guenther et al. model for the period 2080–2100 was 2 $TgC\,a^{-1}$. Niinemets et al. model predicted the lowest emission of the three models throughout the century, and did not respond as strongly as the other models to future climate change, giving a total of 1.58 $TgC\,a^{-1}$. The electron transport system, on which the Niinemets et al. model is based, showed a response of a similar magnitude. On average, 98% increase in isoprene emission was predicted for the period 2080–2100 relative to the emission in the period 1960–1990 with the three emission models.

Of the two monoterpene emission models, Guenther et al. model consistently predicted higher emissions than Niinemets et al. model throughout the 21st century, and responded much more strongly to climate change, perhaps reflecting its higher temperature sensitivity as suggested by Arneth et al. (2007). For the period between 2080 and 2100, Guenther et al. model predicted a total European monoterpene budget of 1.27 $TgC\,a^{-1}$, which represents a 31% increase in monoterpene emissions with re-

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spect to the emissions for the period 1960–1990. Niinemets et al. model predicted a smaller increase in the emissions, giving a total emission from European forests of 1.07 TgC a^{-1}, which represented an 11% increase with respect to the period from 1960 to 1990. As an average of the two models, monoterpene emissions from European forests were predicted to increase by 21% for the period 2080–2100 relative to the period 1960–1990.

4 Discussion

To our knowledge, this is the first time different BVOC emission modelling approaches have been run in parallel on a regional scale. The results serve to both reduce and highlight uncertainty in the modelling of current emissions of isoprene and monoterpenes from European forest species through a two-pronged approach: the compilation and assessment of species specific emission potentials, addressing the broad variability of values published in the literature, and the comparison of three distinct methodologies for the prediction of regional emissions.

To achieve our goals a revised database of isoprene emission factors was constructed for the key tree species growing in European forests using state-of-the art information of species emission potentials (Table 1). So far, all regional emission inventories in Europe have been based on uncritical use of species emission potentials collected in databases that have not been updated since late 90s (e.g., Nick Hewitt's database: http://www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf) (Parra et al., 2004; Projections, 2007; Simpson et al., 1999; Solmon et al., 2004). However, new information has become available on the emission characteristics of some important species such as important Mediterranean species *Quercus suber* that has been traditionally considered "non-emitting" species in emission models. Recent data show that this species strongly emits monoterpenes (Pio et al., 2005; Staudt et al., 2004). Analogously, *Fagus sylvatica*, a dominant component in European temperate deciduous forests has previously been reported to be a minute monoterpene emitter (König et al.,

1995; Steinbrecher et al., 1993), while recent data demonstrated that this species is moderate to high monoterpene emitter (Dindorf et al., 2006; Luchetta, 1999; Moukhtar et al., 2005). While for some species, reliable information of emission potentials is still not available, the aerial coverage of these species is generally small and only minor improvement of large-scale emission estimates is expected.

Model comparisons with tower flux measurements at mid-latitude forest sites show that the models do not differ greatly in their ability to reproduce the short-term variations in isoprene emission, accurately capturing the diurnal time-course of isoprene emission driven by modifications in light and temperature. Guenther et al. model, being solely based on light and temperature, was not effective at capturing the mid-day decline in the emission in drought conditions, leading to a general overestimation of the total emission at the Mediterranean site. The Guenther et al. model is based on two driving variables, and assumes a fixed shape of the response of isoprene emission to these variables. Yet, other factors have been known to affect the emission rates as well (e.g., Affek and Yakir, 2002; Loreto et al., 2001; Loreto and Velikova, 2001; Peñuelas and Llusia 2001; Sharkey and Singsaas, 1995; Sharkey and Yeh, 2001). Given its simplicity, its performance under present-day conditions is surprisingly comparable with the other two more plastic models.

The Niinemets et al. model performed better for simulation of average diurnal emission time-course, but it was unresponsive to the high temperatures experienced in the last few days at the French site. The response of the Niinemets et al. model to temperature was reported in a previous study (Arneth et al., 2007, Fig. 1), though not discussed in detail. There, it was also shown to be slightly less responsive to temperature than the other two models. Martin et al. model, which takes a more detailed approach to describe the limiting precursors of emissions, better reproduced the diurnal time-series, accurately capturing both the day-to-day variability and the average diurnal time-course. Long-term (daily to seasonal) emissions were moderately well reproduced by the models. The low correlation with the data highlights the fact that a complete understanding of emissions drivers and controls is missing from the mod-

els, and we are indeed a long way from fully realistic BVOC emission estimates (Arneth et al., 2008b; Grote and Niinemets, 2008; Monson et al., 2007).

Although there are many strong isoprene and monoterpene emitting tree species in Europe, the regional distribution of these species leads to only a few of these strong emitters being important for the estimation of total European emission budget. These species were not necessarily the strongest emitters, but tended to be species with large coverage in regions with high temperatures and radiation. Total European forest isoprene emissions for the late 20th century were strongly dominated by three *Quercus* species, making up over two thirds of the total isoprene emission. It is therefore of considerable importance to focus research efforts on accurately quantifying the emission potentials from these species, and their emission responses to environmental drivers. Monoterpene emissions were similarly dominated by a few species, with five species contributing 80% of the total emission budget. Having more accurate data on these species could greatly improve the reliability of estimates of present day emission budgets.

The resulting inventory of isoprene emission is similar to the value presented by Simpson et al. (1999) (1.4 $TgC\,a^{-1}$; Simpson et al., Table 18), and Arneth et al. (2008a, 1.2 $TgC\,a^{-1}$) for the same area. Since isoprene emission estimates are highly uncertain, due to their linear dependency on the leaf emission potentials assigned to a species or vegetation type, and due to strong dependence on the kind and quality of the land cover information used (Guenther et al., 2006), the similarity of the calculated annual totals is remarkable. Recently it has been suggested that such agreement between model simulations is due to compensation efforts applied to move model estimates closer to the hypothetical "real" regional or global emission value (Arneth et al., 2008b). We made no such effort, and would suggest that the similarity of different modelled isoprene estimates derives from the fact that regional isoprene emissions are dominated by a few highly emitting and well documented species.

Such similarities do not apply for monoterpene emission estimates, with a broad range of global emissions reported in the literature (Adams et al., 2001; Guenther et

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al., 1995; Kaplan et al., 2006; Lathiere et al., 2006; Levis et al., 1999; Naik et al., 2004; Tao and Jain, 2005; Valdes et al., 2005). Our estimate of total monoterpene emissions from the European forests of 0.97 $TgC\,a^{-1}$ is lower than the emission estimate published in Tao and Jain (2005; 1.73 $TgC\,a^{-1}$). However, their simulation is based on a larger part of Europe than ours, and their parameterization also differs from ours by considering six plant functional types only, rather than species-specific parameterization. To our knowledge, no study has simulated the emission of monoterpenes from European forests on a European scale.

Although both the isoprene and monoterpene emission models performed comparably under current climatic conditions, large differences were observed in the emission estimates for realistic future climatic change scenarios. The differences observed here between model responses for the late 21st century results from the small differences in temperature, radiation and atmospheric CO_2 concentration responses reported in the isoprene model (Arneth et al., 2007, Fig. 1, 2 for review). The isoprene model of Martin et al. is more sensitive to temperature, radiation, and increasing atmospheric CO_2, followed in sensitivity by the Guenther et al. model. The long-term simulations under gradually increasing temperature and atmospheric CO_2 (Fig. 7) highlight the implications of such differences in sensitivities between models. Our study demonstrates that the choice of the model used can greatly alter the final result. The non-concurrence of the emission models in simulations of future scenarios calls into question the validity of numerous conclusions regarding future emissions, and the resulting effects on atmospheric chemistry, made so far on the basis of only one emission model.

A recent study hypothesised that we are overconfident about our ability to accurately model BVOC emissions from terrestrial vegetation, and, according to the terminology of Le Quere (2006), we are in the "illusion" phase of model development (Arneth et al., 2008b). When we consider the estimates of present day emissions that were obtained by applying the same methodology and with the models coupled to the same terrestrial vegetation model, the comparability of model performance does not seem to support such a conclusion. However, when moving to projected future climatic conditions, it

becomes clear that we are far from reaching a clear understanding of the processes governing emission rates (Monson et al., 2007), and their potential responses to future climate change.

Current model development efforts are focused on the improvement of simple empirical algorithms (Guenther et al., 2006) and the development of more process-based emission models (Arneth et al., 2006; Back et al., 2005; Grote et al., 2006; Niinemets et al. 2002a; Martin et al., 2000; Niinemets et al., 1999; Zimmer et al., 2000). Each approach lends itself more easily to different applications, such as the easy implication of simple empirical models in atmospheric chemistry models (e.g., Guenther et al., 2006), or the detailed study allowed for by the more intricate models (e.g., Grote et al., 2006). Despite the big differences in model structures, none of the models included in this study outperformed the others. In fact, no existing approach has been shown to perform consistently better (Arneth et al., 2007). This is due both to a lack of detailed model inter-comparisons, and a lack of good quality data with which to test the models. Further efforts in both fields, together with the development of new modelling approaches and synergies (Grote and Niinemets, 2008; Monson et al., 2007) will be needed to advance our ability to reliably simulate emissions. Meanwhile, we urge that results from different model approaches should be considered in any simulation project dealing with terrestrial emissions of BVOCs, particularly if considering future climate change scenarios.

5 Conclusions

The coupling of the three different model approaches (Guenther et al., Niinemets et al. and Martin et al. models) to an ecophysiological forest model provides a unique opportunity to explore the time-dependent changes in modelled biogenic emissions due to differences in model structure and model responses to changes in climatic and physiological processes. The modelled emissions from present day European forests were shown to be independent of the emission model used, with estimates of 1.03 TgC a^{-1}

for isoprene emission and 0.93 TgC a^{-1} for monoterpenes, giving a consistent emission inventory for BVOCs from European forests. Relative to previous estimates, the differences are moderate and are driven by use of improved emission factor database for 80 European key forest species, as well as implementation on physiological controls on emissions (water stress and phenology).

Coincidence of model estimates of emissions for current and past climatic conditions in Europe suggest that the present day inventories of BVOC emissions provide realistic estimates. However, model-dependent differences in simulated estimates of future emissions of both isoprene and monoterpenes highlight the fact that we are in the early stages of the path towards a full understanding of the processes governing BVOC emissions. This has important implications for any study seeking to model future BVOC emissions. Many studies involving modelled future BVOC emissions (e.g., potential offsetting of emissions by rising CO_2 concentrations, relative effects of changes in land use on quantitative emission estimates, effects on future emissions on tropospheric O_3 concentrations and air quality) may need to be revised to take into account the inherent variability introduced by the choice of the emission model used.

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Table 1. Compilation of isoprene (E_I) and monoterpene (E_M) emission factors and leaf dry mass per unit area (M_A) in 80 dominant species of European forests.

Species[a]	M_A (g m^{-2})[b]	Isoprene		Monoterpenes		
		E_I (μg g^{-1} h^{-1})	Reference	E_M (μg g^{-1} h^{-1})	Light dependency[c]	Reference
Abies alba	185	0	[40], [85]	3	N	[3]
Abies borisii-regis	185	18.4	[35]	2.7	N	[35]
Abies cephalonica	185	0	[d]	3	N	[d]
Acer campestre	95	0	[85], [88]	2	Y	[e]
Acer opalus	57	0	[e]	2	Y	[e]
Acer platanoides	57	0	[34]	2	Y	[e]
Acer spp.	70	0	[26], [51], [85], [88], [99]	2	Y	[15], [51], [99]
Alnus cordata	80	0	[73]	1.5	Y	[52], [88]
Alnus glutinosa	77	0.2	[98]	6.9	Y	[66], [88], [98]
Alnus incana	72	0	[12], [87], [88]	0.6	Y	[30]
Arbutus andrachne	220	0.1	[f]	0.1	Y	[f]
Arbutus unedo	148	0.1	[24], [60], [63], [66], [77]	0.1	Y	[59], [60], [62], [66]
Betula pendula	82	0	[29], [50], [65]	6.7	Y	[28], [29]
Betula pubescens	66	0	[18], [87]	2.6	Y	[28]
Buxus sempervirens	137	11	[59], [61], [62], [64]	0		[59], [62]
Carpinus betulus	80	0	[50]	1.5	Y	[50], [98]
Carpinus orientalis	80	0	[g]	1.5	Y	[g]
Castanea sativa	75	0	[66], [73]	10.9	Y	[66], [73]
Cedrus atlantica	200	0	[73]	0.7	N	[9], [96]
Cedrus deodara	200	0	[9], [73], [96], [97]	0.7	N	[9], [96]
Cupressus sempervirens	250	0.1	[21], [23], [26]	0.7	N	[21], [23], [26]
Eucalyptus spp.	130	38.7	[15], [19], [27], [36], [42], [67], [89], [91]	2.7	N	[15], [26], [36], [57], [67], [89], [91]
Fagus sylvatica	63	0	[50], [70], [75], [88]	8.9	Y	[11], [56], [93], [98]
Fagus sylvatica subsp. *moesiaca*	69	0	[h]	8.9	Y	[h]
Fagus sylvatica subsp. *orientalis*	69	0	[h]	8.9	Y	[h]
Fraxinus angustifolia	80	0	[i]	0		[i]
Fraxinus excelsior	80	0	[37], [65], [88], [98]	0		[37], [88], [98], [65]
Fraxinus ornus	80	0	[i]	0		[i]
Juniperus communis	137	0	[60]	0.7	N	[88]

[a] Species nomenclature follows ARS/GRIN online database (USDA, ARS, National Genetic Resources Program. *Germplasm Resources Information Network - (GRIN)*, National Germplasm Resources Laboratory, Beltsville, Maryland, http://www.ars-grin.gov/cgi-bin/npgs/html/index.pl); [b] based on the original studies and Niinemets (1999) and Wright et al. (2004) (GLOPNET) databases; [c] N – the emission is only controlled by temperature, Y – the emission is controlled by both light and temperature, N/Y(xx) part of the emission is controlled by temperature only, part by both temperature and light. The number in parenthesis shows the percentage of emission controlled by both light and temperature; [d] based on default values for *Abies* that was derived from references [21], [23], [26] for isoprene and [21], [23], [26], [85] for monoterpenes; [e] based on default values for *Acer* that was derived from references [26], [51], [85], [88], [99] for isoprene and [15], [18], [25], [26], [96], [99] for monoterpenes; [f] based on values for *Arbutus unedo*; [g] based on values of *Carpinus betulus*; [h] based on values for *Fagus sylvatica*; [i] based on values for *Fraxinus excelsior*; [j] based on values for *Juniperus oxycedrus and Juniperus phoenicea*; [k] based on values of *Larix decidua*; [l] based on values for *Phillyrea angustifolia*; [m] based on default values for *Pinus* that were derived from [9], [15], [44], [46], [59], [60], [66], [73], [77], [80], [82], [92], [96] for isoprene and [21], [23], [26], [52], [96] for monoterpenes; [n] average values for *Populus alba* and *P. tremula*; [o] average values for *Populus deltoides* and *Populus nigra*; [p] based on values for *Tilia cordata*

Table 1. Continued.

Species[a]	M_A (g m^{-2})[b]	Isoprene		Monoterpenes		
		E_I (μg g^{-1} h^{-1})	Reference	E_M (μg g^{-1} h^{-1})	Light dependency[c]	Reference
Juniperus oxycedrus	141	0	[60], [62], [77]	1.1	N	[60], [62]
Juniperus phoenicea	150	0	[62]	0.6	N	[59], [60], [62]
Juniperus thurifera	150	0	[j]	0.8	N	[j]
Larix decidua	94	0	[40], [88]	8.1	N	[40]
Larix kaempferi	94	0	[k]	8.1	N	[k]
Olea europea	197	0	[2], [59], [62], [66], [96]	0.2	Y	[2], [66], [95], [96]
Ostrya carpinifolia	80	0	[73]	0		[38]
Phillyrea angustifolia	122	0	[62]	0.4	Y	[60]
Phillyrea latifolia	122	0	[l]	0.4	Y	[l]
Picea abies	235	0.6	[22], [31], [43], [84], [98]	1.5	Y/N(30)	[22], [31], [41], [43], [53], [76], [80], [84]
Picea sitchensis	154	6.1	[15], [90]	1	N	[15], [90]
Pinus brutia	250	0	[m]	3	N	[m]
Pinus cembra	250	0	[m]	3	N	[m]
Pinus contorta	250	0	[15]	3	N	[m]
Pinus halepensis	250	0	[9], [62], [63], [96]	1.2	N	[58], [62], [63], [80], [96]
Pinus nigra	250	0	[73]	3	N	[m]
Pinus pinaster	250	0	[37]	1.3	N	[79], [80], [87]
Pinus pinea	169	0	[9], [44], [59], [60], [62], [66], [77], [82], [92], [96]	6.9	Y/N(80)	[9], [44], [59], [60], [62], [66], [74], [77], [82], [92], [96]
Pinus radiata	220	0	[9], [96]	0.8	N	[9], [96]
Pinus strobus	135	0	[73]	3	N	[m]
Pinus sylvestris	230	0	[37], [40], [66], [73], [88]	2.4	Y/N(30)	[41], [49], [78], [80]
Pinus uncinata	91	0	[m]	0.9	N	[13]
Pistacia terebinthus	130	0	[62]	0.5	Y	[61], [62], [64]
Platanus orientalis	100	48.8	[26], [97]	3.9	Y	[57]
Populus alba	89	57.4	[6], [16], [20], [29], [42]	1.2	Y	[66]
Populus alba x P. tremula	88	52.7	[n]	2.9	Y	[n]
Populus nigra	81	60.3	[59], [61], [64], [66], [99]	2.3	Y	[65], [66]
Populus tremula	87	48	[20], [29]	4.6	Y	[29]
Populus x canadensis	64	66.2	[15], [20], [59], [61], [64], [66], [99][o]	2.3	Y	[65], [66][o]
Prunus avium	65	0	[1], [94], [95]	0.2	Y	[2], [94], [95]
Pseudotsuga menziesii	172	1.1	[4], [12], [48]	3.5	N	[12], [14], [54]
Quercus cerris	101	0	[10], [62], [87]	1.6	Y	[10], [60], [62], [64], [71], [87]
Quercus coccifera	167	0	[32], [62]	8.6	Y	[32], [33], [55], [59], [62], [66], [86]
Quercus faginea	125	111	[10]	0.5	Y	[10]
Quercus frainetto	100	90.1	[10], [87]	0		[10], [87]
Quercus ilex	185	0.1	[5], [44], [45], [60], [62], [66], [77], [86], [92]	30.8	Y	[5], [8], [60], [62], [66], [74], [81], [83], [92]
Quercus ithaburensis subsp. *ithaburensis*	100	0.1	[10]	16.2	Y	[10]
Quercus ithaburensis subsp. *macrolepis*	100	0.2	[10]	0.7	Y	[10]
Quercus petraea	129	45.4	[87]	0.5	Y	[50]
Quercus pubescens	101	81	[8], [45], [61], [72]	0.2	Y	[10], [62], [77], [87]
Quercus pyrenaica	101	59	[10]	0.7	Y	[10], [66]
Quercus robur	86	79.3	[40], [69], [88]	0.2	Y	[39], [40], [88]
Quercus rubra	99	58.2	[17], [20]	0.9	Y	[15], [51]
Quercus suber	157	0	[66], [71], [73], [77], [87]	21.4	Y	[68], [83]
Quercus trojana	140	0.2	[10]	0.2	Y	[10]
Robinia pseudoacacia	64	24.8	[21], [47], [51], [96]	4	Y	[47], [51], [57], [96]
Salix alba	99	20.9	[62], [66]	1.1	Y	[66]
Sorbus aucuparia	63	0	[40], [88]	0		[40], [88]
Tilia cordata	76	0	[73], [88]	0		[88]
Tilia platyphyllos	76	0	[p]	0		[p]
Tsuga spp.	123	0	[12], [26]	1.5	N	[7], [12]

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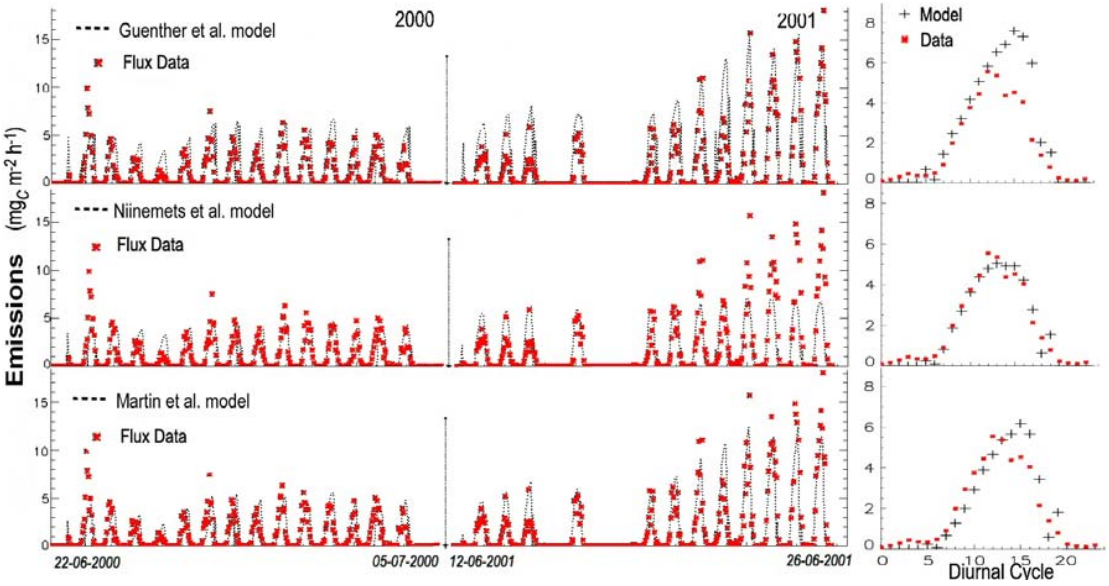

Fig. 1. Hourly measured canopy isoprene emissions ($mg_C\ m^{-2}\ h^{-1}$), from the French site for two two-week periods in 2000 and 2001 (Arneth et al., 2007), compared with the simulation results using GOTILWA+ with the three isoprene emission models (Guenther et al., Niinemets et al., and Martin et al. models). The average diurnal time-course from the measurements is also compared with the simulation results.

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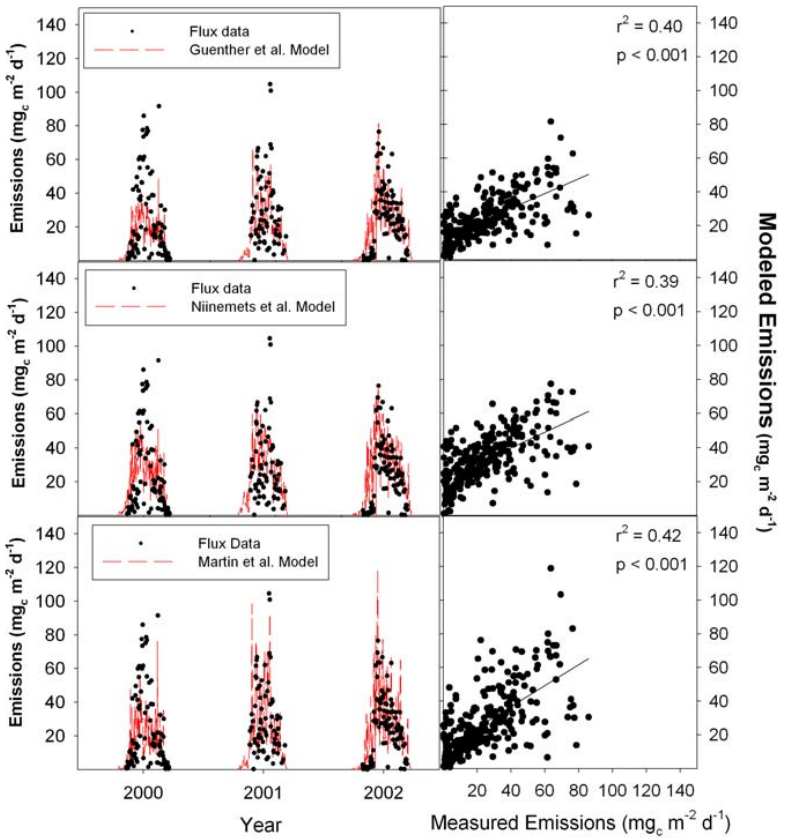

Fig. 2. Comparison of daily integrated canopy isoprene emission fluxes from the UMBS forest (Pressley et al., 2005) and fluxes simulated by GOTILWA+ with the three emission models compared (Guenther et al., Niinemets et al., and Martin et al. models) over three years (left panels) and the regressions of measurements vs. simulations (right panels).

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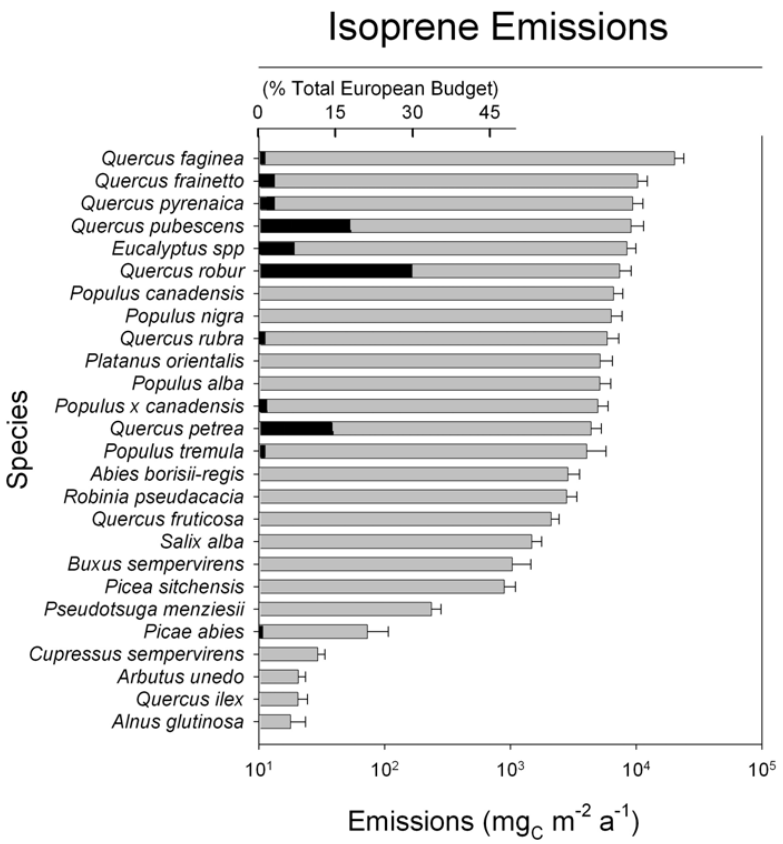

Fig. 3. Estimated average annual isoprene emissions (log scale) from European forest canopies for the period 1960–1990 (grey bars). Values represent average estimates from the three emissions models (Guenther et al., Niinemets et al., and Martin et al.). Black bars denote the percent contribution of each species to the total European isoprene emissions budget for this period (for contributions of greater than 1%). Species emission potentials are according to Table 1.

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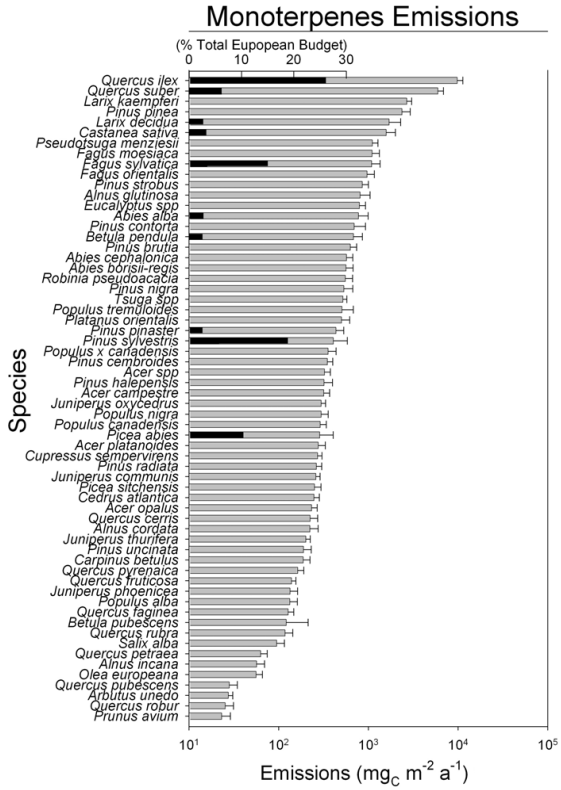

Fig. 4. Estimated average annual monoterpene emissions ($mg_C\ m^{-2}\ a^{-1}$) from European forest species for the period 1960–1990 (grey bars). Values represent average estimates from the two emissions models (Guenther et al., and Niinemets et al.). Black bars denote the percent contribution to total European monoterpene emissions budget for this period (for contributions of greater than 1%). Species emission potentials follow Table 1.

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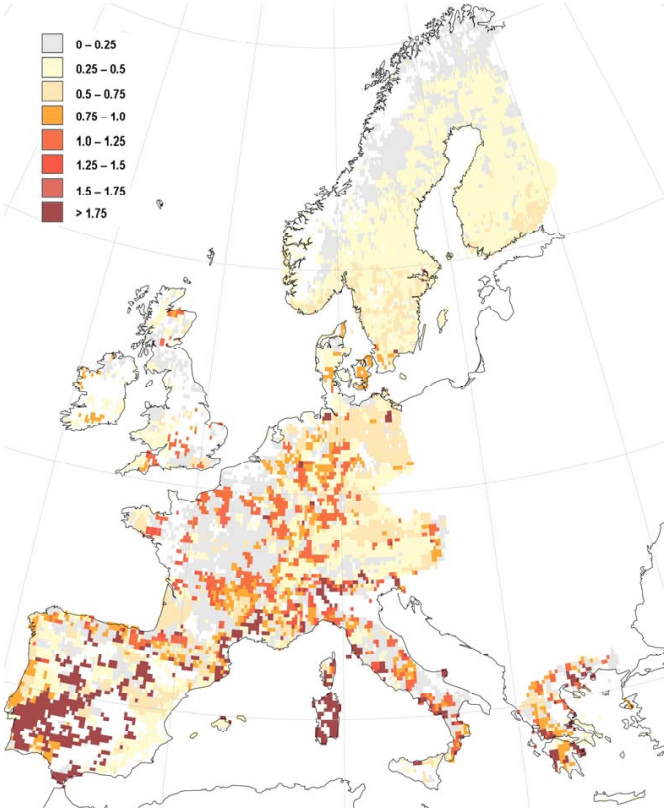

Fig. 5. Estimated annual isoprene emissions ($gC\,m^{-2}\,a^{-1}$) from European forests over the period 1960–1990, using average estimates from the three isoprene emissions models coupled to GOTILWA+.

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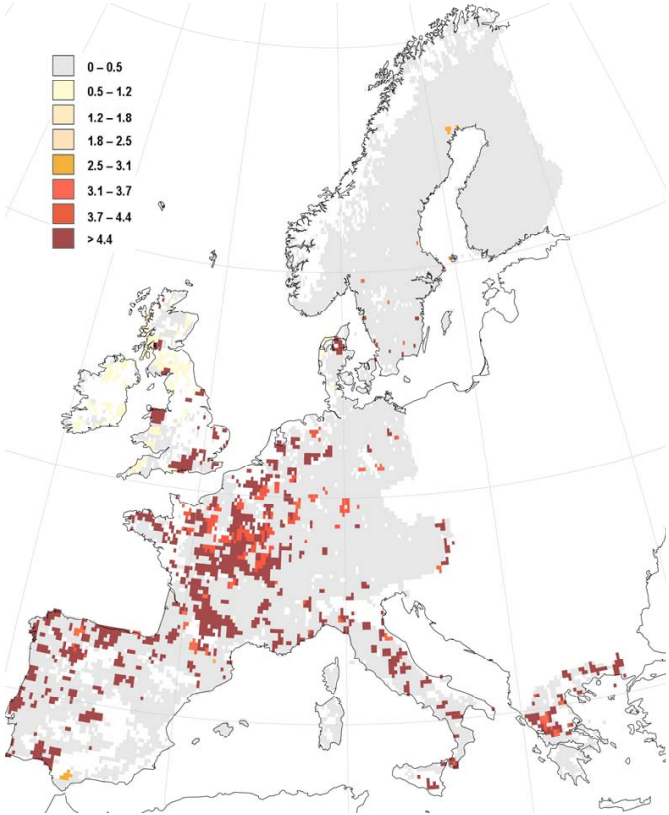

Fig. 6. Estimated annual monoterpene emissions (gC m^{-2} a^{-1}) from European forest canopies over the period 1960–1990, using average estimates from the two monoterpene emission models (Guenther et al. and Niinemets et al.) coupled to GOTILWA+.

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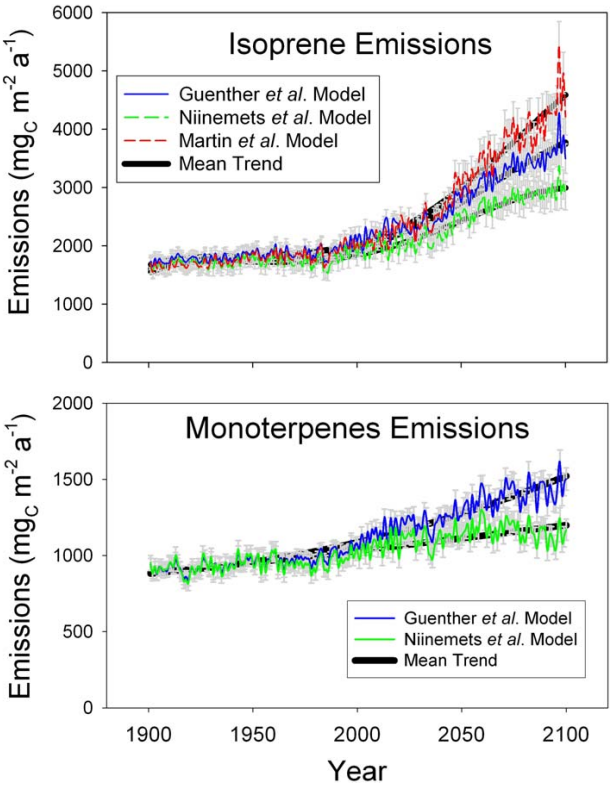

Fig. 7. Average per m^2 modelled isoprene and monoterpenes emissions from European forest canopies from 1900 to 2100. Climate from the CRU (New et al., 1999) was used for the period 1900 to 2000. Results from 2001 to 2100 correspond to climate from HadCM3 global circulation model using climate change scenario A2 (IPCC, 2001, 2007). The displayed error bars (in grey) represent the standard error from the mean. The Mean Trend is a quadratic regression ($y=y_0+ax+bx^2$) of the displayed data.

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