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Seasonality of monoterpene emission potentials in *Quercus ilex* and *Pinus pinea*: Implications for regional VOC emissions modeling

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[1] VOC emissions from terrestrial ecosystems provide one of the principal controls over oxidative photochemistry in the lower atmosphere and the resulting air pollution. Such atmospheric processes have strong seasonal cycles. Although similar seasonal cycles in VOC emissions from terrestrial ecosystems have been reported, regional emissions inventories generally omit the effect of seasonality on emissions. We compiled measurement data on seasonal variations in monoterpene emissions potentials for two evergreen species (*Quercus ilex* and *Pinus pinea*) and used these data to construct two contrasting seasonal response functions for the inclusion in monoterpene emission models. We included these responses in the Niinemets et al. model and compared simulation results to those of the MEGAN model, both with and without its predicted seasonality. The effect of seasonality on regional monoterpene emissions inventories for European Mediterranean forests dominated by these species was tested for both models, using the GOTILWA+ biosphere model platform. The consideration of seasonality in the Niinemets et al. model reduced total estimated annual monoterpene emissions by up to 65% in some regions, with largest reductions at lower latitudes. The MEGAN model demonstrated a much weaker seasonal response than that in the Niinemets et al. model, and did not capture the between species seasonality differences found in this study. Results suggest that previous regional model inventories based on one fixed emission factor likely overestimate regional emissions, and species-specific expressions of seasonality may be necessary. The consideration of seasonality both largely reduces monoterpene emissions estimates, and changes their expected seasonal distribution.

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1. Introduction

[2] Nonmethane biogenic volatile organic compounds (VOCs) represent a heterogeneous compound class made up of a wide range of reactive hydrocarbons (isoprene, monoterpenes, and sesquiterpenes) emitted by most plant species. VOC emissions from terrestrial ecosystems provide one of the principal controls over oxidative photochemistry in the lower atmosphere [*Fehsenfeld et al.*, 1992; *Crutzen et al.*, 1999; *Monson and Holland*, 2001] and have a large impact on local air pollution [e.g., *Fuentes et al.*, 2000; *Kanakidou et al.*, 2005; *Helmig et al.*, 2006; *Szidat et al.*, 2006; *Gelencsér et al.*, 2007]. The air chemistry and air pollution impacts of VOCs depend on the availability of reaction partners, e.g., reactive nitrogen compounds, which have a regionally specific seasonal pattern that is driven by anthropogenic as well as biological activities [e.g., *Pierce et al.*, 1998; *Fiore et al.*, 2005; *Tie et al.*, 2006]. Thus, it is not only the overall total emission budget but also the timing of emissions that is important.

[3] Natural seasonal cycles are known to have a strong control over the timing of VOC emissions [e.g., *Llusià and Peñuelas*, 2000; *Hakola et al.*, 2003, 2006; *Holzinger et al.*, 2006]. Climate change already affects seasonal cycles in terrestrial ecosystems, most notably the timing and duration of phenological events such as the onset of budburst and the rates of foliage development and senescence [*Peñuelas and Filella*, 2001; *Bakkenes et al.*, 2002; *Peñuelas et al.*, 2002; *Walther et al.*, 2002] and is likely to continue to do so in the future [*Gitay et al.*, 2001; *Prieto et al.*, 2009]. Compared to other regions, Mediterranean regions in particular are threatened by such changes in the near future due to proportionally higher projected increases in temperature [*Giorgi et al.*, 2004; *Giorgi*, 2006; *Beniston et al.*, 2007; *Intergovernmental Panel on Climate Change* (*IPCC*), 2007], and the potential for drought-driven phenological shifts in response to changes in precipitation [*Peñuelas et al.*, 2004]. Moreover, many dominant ecosystems of the

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Mediterranean regions contain species that are strong VOC emitters such as the Mediterranean evergreen oak *Quercus ilex* L. dominated forests, which emit high amounts of highly reactive monoterpenes and exhibit a strong seasonality [*Llusià and Peñuelas*, 2000]. It is not entirely clear why plants emit VOCs, their presence has been reported to increase plant tolerance to several environmental stresses, i.e., high temperatures (see *Sharkey et al.* [2007] for a review). Future changes in environmental conditions are likely to change VOC emissions not only directly through altered temperature effects on the emission rates, but also indirectly due to altered seasonal cycles such as phonological events or enzyme activities. Understanding the overall effect of seasonal cycles on emissions (and potential future changes) is thus necessary to reduce uncertainty in current estimates and future projections of VOC emissions.

[4] Various models exist to describe the emissions of VOCs from terrestrial vegetation scales (see *Arneth et al.* [2008b] and *Grote and Niinemets* [2008] for recent reviews). These models are based on the observed short-term response of emissions to temperature and light intensity. Due to a lack of long-term seasonal measurement data, they have a bias toward employing only a snapshot of whole season, typically midseason measurements, for the parameterization and calculation of the basal emission factor (see below) (for representative emission inventories in midseason used in major scaling exercises see *Kesselmeier and Staudt* [1999], *Simpson et al.* [1999], and *Geron et al.* [2000, 2006]). Other processes, operating over longer time scales, such as the effect of seasonality, and potential effects of CO_2 fertilization have received little attention. Atmospheric CO_2 concentration changes have been suggested to modify the emission response on the decadal or longer time scale [*Possell et al.*, 2005; *Arneth et al.*, 2007a, 2007b, 2008a]. The determination of seasonality effects is lately receiving more attention as an important factor in regional budgets [*Simon et al.*, 2006; *Tarvainen et al.*, 2007], and represents a major uncertainty in biogenic emission simulations [*Funk et al.*, 2005; *Monson et al.*, 2007; *Arneth et al.*, 2008b].

[5] Seasonality in emissions has been suggested to affect the plant species–specific emission factor. This factor describes the potential for emissions during the measurement period, often during the midsummer and optimal conditions. It is the most important factor for the description of VOC emissions [*Arneth et al.*, 2008b; *Grote and Niinemets*, 2008] and varies strongly among species from values near zero to greater than 100 $\mu g\ g_{leaf}^{-1}\ h^{-1}$ [*Kesselmeier and Staudt*, 1999; *Wiedinmyer et al.*, 2004]. The basal emission factor is known to change considerably during the year [e.g., *Llusià and Peñuelas*, 2000; *Staudt et al.*, 2002; *Hakola et al.*, 2006; *Holzinger et al.*, 2006]. The mechanisms behind this change are not fully understood, but it has been suggested to be due to the production and destruction of enzymes that are responsible for the formation of VOCs [*Lehning et al.*, 1999; *Loreto et al.*, 2001; *Mayrhofer et al.*, 2005]. In large-scale simulated emission estimates, the seasonal dynamics generated by such physiological preconditioning is almost always neglected. The influence of the omission of seasonal variation in emission potential on regional VOC emission budgets has yet to be quantified.

[6] Few approaches have been developed to simulate this seasonal modification of emissions. *Geron et al.* [2000] applied a weak seasonality using the integrated temperature of the previous 18 h instead of instantaneous temperature. *Fuentes and Wang* [1999] used an empirical function based on cumulated temperature or growing degree days, respectively, and *He et al.* [2000] varied the emission factor in dependence on the number of monthly sunshine hours, and *Schaab et al.* [2003] used a nonsymmetrical response curve. Only one regionally applied model known to the authors, the *Guenther et al.* [2006] MEGAN model, explicitly accounts for the seasonal cycle of emissions on the regional scale. This model applies the same empirical adjustment to all plant functional types, based on the light and temperature regime of the past 10 days.

[7] These models have typically resulted in bell-shaped response curves of VOC emissions during the season, reflecting seasonal variation in light and temperature. However, the application of relatively short-term previous integrated climate to describe seasonal variation assumes that seasonal modifications mainly reflect acclimation response of foliage emission potentials. While environmental modifications can trigger the onset of seasonal events such as bud break or leaf senescence, the control of phenological events by climatic drivers alone is not often strong [*Battey*, 2000]. Seasonal variation in VOC emissions is thus often not bell-shaped [*Llusià and Peñuelas*, 2000], reflecting stronger variation of emissions than predicted by integrated climatic variables, possibly due to direct triggering by phenological events and the seasonal course of enzyme activity [*Lehning et al.*, 2001], as simulated by the detailed SIM-BIM2 model [*Grote et al.*, 2006]. The scarcity of whole season emission data has hindered the inclusion of such species controls into the emission models.

[8] The overall uncertainty in our knowledge of the drivers of seasonal dynamics of emissions, and how to model them, is potentially a large source of error when modeling VOC emissions from terrestrial vegetation. In this paper, we focus on monoterpenes (a class of VOCs that consist of two isoprene units and have the molecular formula $C_{10}H_{16}$), and addressed the problem of seasonal dynamics of monoterpene emission potentials by developing seasonal emission factor response functions for two key species in Mediterranean forest ecosystems: the broadleaved evergreen sclerophyll *Quercus ilex* and the evergreen conifer *Pinus pinea*. The response functions were integrated into the *Niinemets et al.* [1999, 2002] monoterpene emission model coupled to the process-based terrestrial biogeochemical model GOTILWA+ [*Gracia et al.*, 1999; *Keenan et al.*, 2008, 2009a]. Simulations were run for these two dominating species over the European Mediterranean region to quantify the effect of the consideration of a seasonally dynamic emissions potential on the total emissions budget for these two species. The simulations were further compared with simulations coupling the commonly used empirical *Guenther et al.* [2006] model development, MEGAN, both with and without its seasonal modifications of emissions, to the GOTILWA+ model.

2. Models, Measurements, and Methods

2.1. Studied Species

[9] The Holm oak (*Quercus ilex*) is an evergreen sclerophyllous tree native to Mediterranean Europe. It is a strong

emitter of monoterpene species (mostly α-pinene, β-pinene, sabinene, myrcene, and limonene), and although its distribution is limited to the Mediterranean region, it contributes more than 25% of the total European forest monoterpene emissions budget [*Keenan et al.*, 2009a]. The aerial coverage of *Quercus ilex* is currently increasing in some mesic areas as the result of warmer temperature and reductions in water availability [*Peñuelas and Boada*, 2003]. The Italian stone pine (*Pinus pinea*) is an evergreen conifer widespread in the European Mediterranean region. It is also one of the strongest monoterpene emitters of European forest species (emitting mostly linalool, trans-β-ocimene, α-pinene, myrcene, and limonene, among others). We assume no emissions from storage ducts, as in both species, the bulk of monoterpenes are emitted in a temperature- and light-dependent manner [*Bertin et al.*, 1997; *Staudt et al.*, 1997].

2.2. Biosphere Model Platform Description

[10] To describe canopy-level emissions, and scale the leaf-level monoterpene emission models to the region, we coupled both the Niinemets et al. and the MEGAN model monoterpene emission models to the process based terrestrial biogeochemical model GOTILWA+ (Growth Of Trees Is Limited by WAter) [*Gracia et al.*, 1999; *Keenan et al.*, 2008, 2009b].

[11] The GOTILWA+ model describes leaf structural and chemical characteristics, and thus foliage physiological potentials. The model also describes the forest structure and the microclimatic conditions necessary to scale from the leaf to the canopy, and for correct integration of fluxes distinguishes between sunlit and shaded leaf fractions [*Wang and Leuning*, 1998; *Dai et al.*, 2004; *Niinemets and Anten*, 2009]. The distribution of intercepted diffuse and direct radiation within the canopy depends on the time of the day, season, and the area of leaf exposed to the sun [*Campbell*, 1986]. The photosynthetic module couples the *Farquhar et al.* [1980] photosynthesis model, with dependencies on intercepted radiation, species-specific photosynthetic capacities, leaf temperature, and leaf intercellular CO_2 concentration (C_i), to the *Leuning et al.* [1995] stomatal conductance model, that is the advancement of the *Ball et al.* [1987] model.

[12] To scale from the canopy to the region, an extensive database has been built within the framework of the European ATEAM (Advanced Terrestrial Ecosystem Analysis and Modeling) and ALARM (Assessing Large-scale Risks for biodiversity with tested Methods) projects [*Keenan et al.*, 2009a], connecting diverse information sources at a European level and adapting them to fit the same spatial resolution of 10′ latitude × 10′ longitude (minutes). The database contains data related to forest species, forest coverage, forest structure, forest function (photosynthesis, respiration rates), soil hydrology, organic matter decomposition rates and management strategies [*Schröter et al.*, 2005]. The species distribution database was updated using distribution data compiled by members of the EUFORGEN network [*Fady and Vendramin*, 2004] (www.euforgen.org, updated 2008). The model setup used to scale from the leaf to the region has previously been described by *Keenan et al.* [2009a].

2.3. Leaf-Level Monoterpene Emissions Algorithms

[13] We considered the two leaf-level monoterpene emission models most commonly applied to estimate monoterpene emissions on the regional scale. Both models take contrasting approaches to modeling emissions, each with different assumptions about the way in which environmental factors limit the emissions and with different levels of mechanistic detail. Where pertinent, modifications were made for consistency between these models (as in work by *Arneth et al.* [2007a]). No direct CO_2 or water stress effect on the emissions was applied in this modeling exercise.

2.3.1. MEGAN Model

[14] The most widely used model for the simulation of natural VOC emissions was developed by *Guenther et al.* [1991, 1993]. Its wide use is in large part due to its simplicity, describing emission rates by varying a long-term basal emission factor for monoterpenes (E_M) in dependence on light and temperature. These adjustments are applied through two empirical factors, one describing the response to light intensity and the other to leaf temperature, using the following algorithm:

$$E = E_M C_L C_T. \tag{1}$$

The emission factor, E_M, used in the model is the emission rate normalized to a leaf temperature (T) of 30°C and quantum flux density (Q) of 1000 μmol m^{-2} s^{-1} [*Guenther et al.*, 1991, 1993, 1995; *Guenther*, 1997]. C_L and C_T are the functions of quantum flux density and leaf temperature, respectively) as outlined in the *Guenther et al.* [2006] MEGAN (Modeling Emissions of Gases and Aerosols from Nature) model version. Parameters were determined following the original parameterizations of the Guenther et al. model, including recent algorithms developed in MEGAN, which links parameter values to short-term (24 h) and long-term (10 days) fluctuations in temperature and light intensity [*Müller et al.*, 2008]. For simulations using MEGAN without accounting for seasonality, the parameterization for long-term fluctuations was omitted.

[15] Other specifications of the MEGAN model, such as the effect of water stress, have been omitted in this study to ensure comparability with the *Niinemets et al.* [1999, 2002] model (both MEGAN and the Niinemets et al. model assume no leaf age affect for evergreen species). The seasonal cycle of emissions in the MEGAN model is based on the previous 10 days light and temperature. It has been previously calibrated [*Guenther et al.*, 2006] using emission data from five studies (not included in response function parameterization derived in this study) [*Petron et al.*, 2001; *Monson et al.*, 1994; *Sharkey et al.*, 1999; *Geron et al.*, 2000; *Hanson and Sharkey*, 2001], including four different species (*Quercus alba, Quercus rubra, Quercus macrocarpa*, and *Populus tremuloides*).

2.3.2. Niinemets et al. Model

[16] In the *Niinemets et al.* [1999, 2002] model for monoterpene emissions the supply of dimethylallyldiphosphate (DMADP) and Nicotinamide adenine dinucleotide phosphate (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

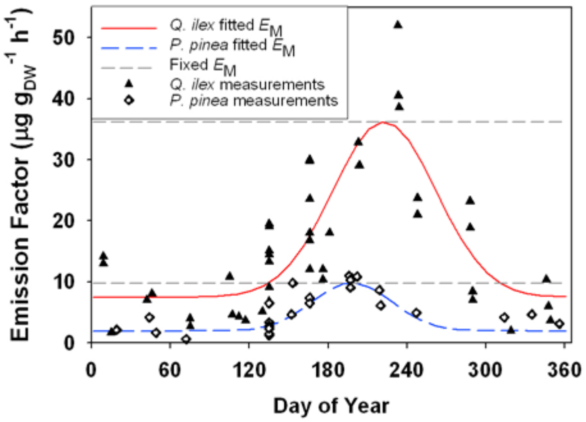

Figure 1. Seasonal variation in monoterpene emission factor (E_M) in the Mediterranean evergreen sclerophyll *Quercus ilex* and the evergreen conifer *Pinus pinea*. Data were fitted by equation (2). (See section 2.4. for data sources and curve parameters.)

controlling factors for the rate of monoterpene synthesis. Thus the emission rates are linked to the activity of the synthase enzyme S_S to predict the capacity of the synthesis pathway and to foliar photosynthetic metabolism via the photosynthetic electron transport rate, J, to predict substrate availability for monoterpene synthesis [*Niinemets et al.*, 1999, 2002].

[17] Emission rates are calculated through the rate of photosynthetic electron transport, the fraction of total electron flow used for the monoterpene synthesis, and the cost of monoterpene synthesis in terms of electrons. Emissions can thus be linked to the photosynthetic electron transport activity of the leaf with the use of only one single leaf dependent parameter: the fractional allocation of electron transport to monoterpene synthesis.

2.4. Derivation and Implementation of Seasonal Response Functions

[18] An extensive literature search was performed to identify measurements related to the seasonal variation of the basal monoterpene emission factor (E_M). Data were compiled from studies explicitly looking at seasonal variation in E_M as well as from studies reporting emission rates for several sampling events during the growing season where the measurement date was reported. In all cases, only measurements from fully sun-exposed branches were included. For *Quercus ilex*, E_M estimates were obtained from *Bertin et al.* [1997], *Owen et al.* [1997], *Kesselmeier et al.* [1997], *Street et al.* [1997], *Kesselmeier et al.* [1998], *Llusià and Peñuelas* [2000], and *Staudt et al.* [2004]. For *Pinus pinea*, E_M estimates were obtained from *Pio et al.* [1993], *Kesselmeier et al.* [1997], *Owen et al.* [1997], *Staudt et al.* [1997], *Street et al.* [1997], *Owen and Hewitt* [2000], *Staudt et al.* [2000], *Owen et al.* [2001], *Sabillón and Cremades* [2001]. The compiled data for both species exhibited a curve with a maximum between days 200–320 (Figure 1) and were fitted by different empirical functions. The best fit was obtained by an asymmetric exponential function that allows for different rates of increase and reduction in E_M during the growing season [*June et al.*, 2004] to describe the seasonal variation in E_M:

$$E_M = E_0 + E_{max} e^{-\left[\frac{(D - D_{max})}{\varepsilon}\right]^2}, \qquad (2)$$

where E_0 is the minimum and E_{max} the maximum emission rate during the season, D is the day of the year, D_{max} is the day at E_{max}, and ε determines the rate of change of E_M during the season. The data were fitted by equation 2 through minimizing the least squares between the measurements and predictions, resulting in a high degree of correlation between the measured and predicted values ($r = 0.83$ for *Quercus ilex* and $r = 0.86$ for *Pinus pinea*) (see Figure 1 for the fits). For *Quercus ilex*, the model parameters obtained were: $E_0 = 7.49$ μg g^{-1} h^{-1}, $E_{max} = 28.8$ μg g^{-1} h^{-1}, $D_{max} = 222.7$, $\varepsilon = 55.6$, while for *Pinus pinea* $E_0 = 1.95$ μg g^{-1} h^{-1}, $E_{max} = 7.90$ μg g^{-1} h^{-1}, $D_{max} = 198.1$, $\varepsilon = 42.9$.

2.5. Modeling Protocol

[19] Simulations were run with each emission model coupled to the GOTILWA+ model for each 10’ longitude x 10’ latitude scale pixel containing *Quercus ilex* or *Pinus pinea* forests in the European Mediterranean region. For parameterization of the forest structural components in GOTILWA+, species-specific parameters for *Quercus ilex* and *Pinus pinea* were applied. Two versions of the Niinemets et al. model were considered: one with a fixed tree species-specific emissions potential (Figure 1), and the other varying the emissions potential using the seasonally dynamic response derived in Section 2.4 (Figure 1). Two versions of the MEGAN model were also used: one without the seasonal parameter modification (see Section 2.3.1), and the other applying the MEGAN seasonal modification (based on the previous light and temperature regime). For each tree species, simulations were performed for years from 1900 to 2000, using the reconstructed climatic time series based on the CRU05 (1901–2000) monthly data set [*New et al.*, 1999], with atmospheric concentrations of CO_2 from 1901 to 2000 obtained from the Carbon Cycle Model Linkage Project [*McGuire et al.*, 2001]. The presented results correspond to the 1960 to 1990 time period.

3. Results

[20] The application of seasonal variations in monoterpene emissions in both models had a large affect on both the total monoterpene emissions budget and the timing of monoterpene emissions for the two tree species (Table 1). For both species the consideration of a seasonally changing emission potential with the Niinemets et al. model reduced the total annual monoterpene emissions from the European Mediterranean region by roughly 50%, when compared to emission estimates from the Niinemets et al. model with a fixed basal emission factor at E_{max}. The difference between the seasonal and nonseasonal MEGAN model was not as strong, with an overall difference in annual emissions of 21% over the two species (Table 1).

[21] Emissions from winter, early spring and late autumn were most affected. In the case of the seasonal Niinemets et al. model, the highest emissions potential was not reached until late summer for *Quercus ilex* (Figure 2) and midsummer for *Pinus pinea* (Figure 3). For the seasonal MEGAN model,

Table 1. Average Monoterpene Emissions for the Niinemets et al. and MEGAN Models for *Quercus ilex* and *Pinus pinea* During the Years 1960–1990[a]

	Quercus ilex Emissions (g_C m^{-2} $month^{-1}$)						*Pinus pinea* Emissions (g_C m^{-2} $month^{-1}$)					
	MEGAN Model			Niinemets et al. Model			MEGAN Model			Niinemets et al. Model		
Period	Nonseasonal	Seasonal	Reduction (%)	Nonseasonal	Seasonal	Reduction (%)	Nonseasonal	Seasonal	Reduction (%)	Nonseasonal	Seasonal	Reduction (%)
JFM	0.23	0.10	55.4	0.28	0.06	88.6	0.06	0.04	38.9	0.1	0.02	80
AMJ	0.73	0.54	25.5	0.87	0.33	62.1	0.18	0.13	28.3	0.24	0.11	54.2
JAS	1.30	1.20	7.5	1.06	0.91	14.2	0.31	0.27	11.7	0.27	0.18	33.3
OND	0.33	0.21	37.7	0.41	0.13	68.3	0.08	0.07	20.7	0.14	0.03	78.6
Totals	2.59	2.05	20.8	2.62	1.43	45.4	0.63	0.51	20.1	0.75	0.34	54.7

[a] For the Periods January-February-March (JFM), April-May-June (AMJ), July-August-September (JAS), and October-November-December (OND). Niinemets et al. model is from *Niinemets et al.* [1999, 2002] and MEGAN model is from *Guenther et al.* [2006]. Average monoterpene emissions given in g_C m^{-2} $month^{-1}$. Emissions for the MEGAN model and Niinemets et al. model are compared both with and without a seasonal adjustment. The percentage reduction refers to the reduction in total emissions from each model due to the implication of a seasonal variation in emissions.

highest emissions were in late summer for both species. The MEGAN model predicted only very small reduction in emissions due to seasonality in autumn, due to the fact that it uses the past 10 days light and temperature, which allows high emissions to be sustained after optimum summer conditions.

[22] For *Quercus ilex*, the nonseasonal versions of both models gave very similar annual monoterpene emissions totals. There were large differences within the year however. For the nonseasonal models, the Niinemets et al. model gave higher emissions in the early and later parts or the year, and the MEGAN model giving higher peak emissions during summer (Table 1). The implication of a seasonal variation in emission potentials in the Niinemets et al. model explained much of the difference in the shape of the annual emission response when compared to the MEGAN model (Figure 2).

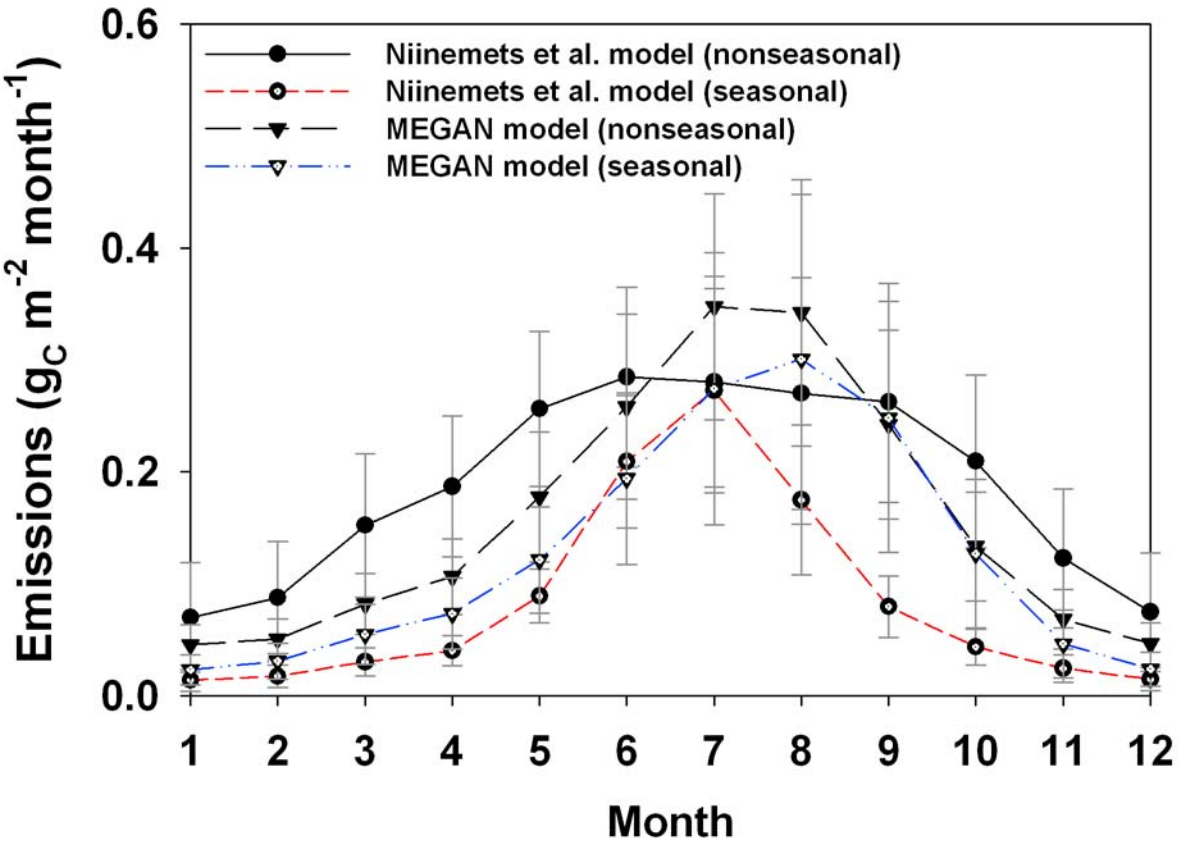

Figure 2. Average monthly per pixel forest canopy monoterpene emissions (g_C m^{-2} $month^{-1}$) with the *Niinemets et al.* [1999, 2002] model and the MEGAN model [*Guenther et al.*, 2006] coupled to the GOTILWA+ model [*Gracia et al.*, 1999; *Keenan et al.*, 2009a], for Mediterranean Europe *Quercus ilex* dominated forests over the period 1960–1990. The Niinemets et al. model is run both with and without the seasonality factor (Figure 1). The MEGAN model is run both with and without its measure of seasonality.

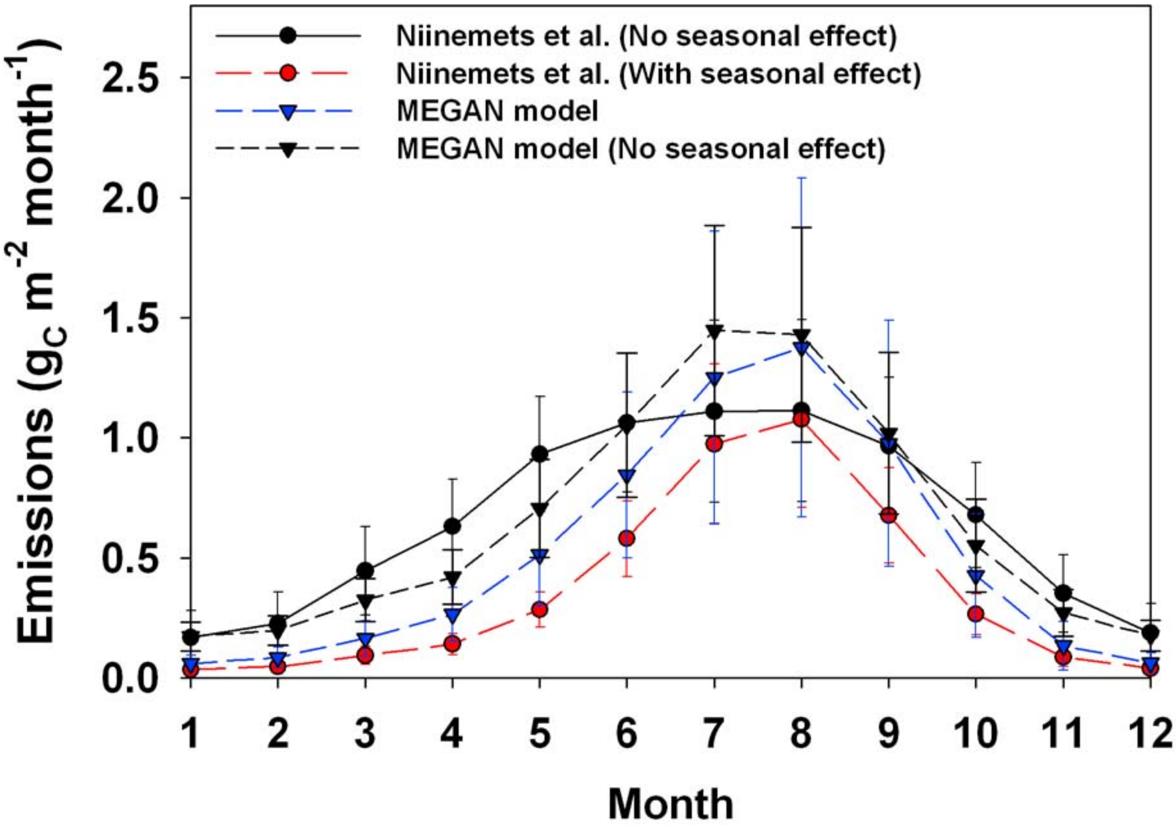

Figure 3. Average monthly per pixel forest canopy monoterpene emissions (g_C m^{-2} $month^{-1}$) with the *Niinemets et al.* [1999, 2002] model and MEGAN model [*Guenther et al.*, 2006] coupled to the GOTILWA+ model [*Gracia et al.*, 1999; *Keenan et al.*, 2009a], for Mediterranean Europe *Pinus pinea* dominated forests over the period 1960–1990. The Niinemets et al. model is run both with and without the seasonality factor. The MEGAN model is run both with and without its measure of seasonality.

The seasonal MEGAN model showed the same shape as the seasonally dynamic Niinemets et al. model, with peak emissions around August (Figure 2), but gave higher emissions than those of the seasonal Niinemets et al. model at all times during the year (Table 1). The total annual emissions budget with the seasonal MEGAN model for *Quercus ilex* over the Mediterranean region was 43% higher than that of the seasonal Niinemets et al. model (Table 1).

[23] For *Pinus pinea,* the nonseasonal Niinemets et al. model and the nonseasonal MEGAN model again gave similar annual totals (differing by 16%), with a very different distribution of monoterpene emissions within the year. The distribution of monoterpene emissions within the year from the seasonally dynamic Niinemets et al. model was also more comparable to both the nonseasonal and the seasonal MEGAN models than was the nonseasonal Niinemets et al. model (Figure 3). Much of the difference between the original Niinemets et al. model and the seasonal MEGAN model was explained by the inclusion of a seasonally dynamic emissions factor in the Niinemets et al. model, particularly in spring and early summer (Table 1). Marked differences appear in late summer and autumn, with monoterpene emissions from the seasonal MEGAN model (which applies the same seasonal response to both species) peaking much later than those of the seasonally dynamic Niinemets et al. model. This leads to 56% higher emissions in the second half of the year with the seasonal MEGAN model (Table 1). The seasonal MEGAN model gave 50% higher total annual emissions than the seasonal Niinemets et al. model.

[24] The impact of the consideration of a seasonally dynamic emission potential on the total annual monoterpene emission budget from the Niinemets et al. model was higher at lower latitudes. The reduction in the total annual monoterpene emissions from the Niinemets et al. model due to the consideration of seasonal variability in the basal emission factor varied from 25% (in the region of the Pyrenees Mountains), to 65% (in the southern Iberian Peninsula). This trend was reflected in both *Quercus ilex* (Figure 4a) and in *Pinus pinea* (Figure 5a). Overall, the impact of seasonal variation in the Niinemets et al. model was higher in *Pinus pinea*, which shows a stronger seasonal cycle in its emission potential (a 5.2 fold increase over a 62 day period, compared to a 4.8 fold increase over a 98 day period for *Quercus ilex* (Figure 1)). Areas subject to warmer winters showed the largest differences.

[25] The difference between the MEGAN model with and without seasonality was considerably smaller than that observed with the Niinemets et al. model (Figures 4 and 5), suggesting that the measure of seasonality in the MEGAN model is much weaker than that derived from the data in Section 2.4. The difference in total annual monoterpene

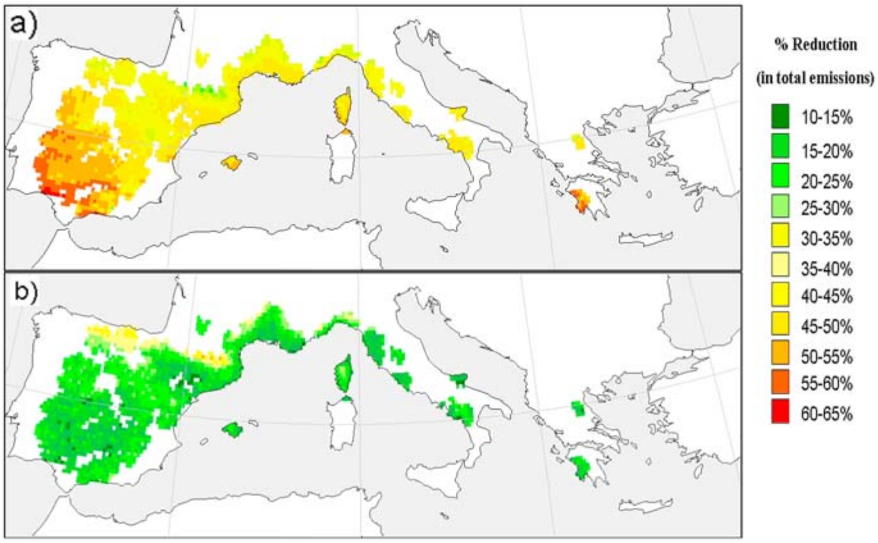

Figure 4. Average regional differences (percent) in total simulated annual monoterpene emissions: (a) between the *Niinemets et al.* [1999, 2002] seasonal and nonseasonal model and (b) the MEGAN model [*Guenther et al.*, 2006] with and without its seasonal response. Both models are run coupled to the GOTILWA+ model [*Gracia et al.*, 1999; *Keenan et al.*, 2009a], for *Quercus ilex* forests in the Mediterranean Europe region, for the period 1960–1990.

emissions did not show a strong latitudinal response, due to the fact that the seasonal response in the MEGAN model is based on temperature and light.

4. Discussion

[26] Seasonal variation in VOC emissions in Mediterranean plants has been widely reported [e.g., *Grinspoon et al.*, 1991; *Fuentes et al.*, 1995; *Staudt et al.*, 1997; *Fuentes and Wang*, 1999; *Lehning et al.*, 1999; *Peñuelas and Llusià*, 1999; *Llusià and Peñuelas*, 1999; *Loreto et al.*, 2001; *Kuhn et al.*, 2004; *Mayrhofer et al.*, 2005]. Accounting for such seasonal changes in monoterpene emissions has been shown here to have a large impact on modeling the seasonal dynamics of emissions. The presented study is the first to demonstrate the importance of considering the seasonal dynamics of monoterpene emissions on a regional scale, and illustrates the magnitude that the consideration of

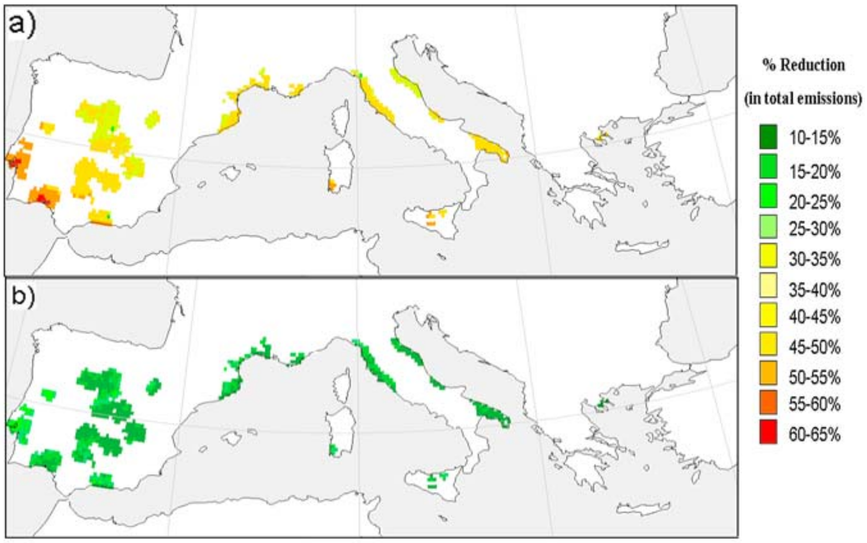

Figure 5. Average regional differences (percent) in total simulated annual monoterpene emissions: (a) between the *Niinemets et al.* [1999, 2002] seasonal and nonseasonal model and (b) the MEGAN model [*Guenther et al.*, 2006] with and without its seasonal response. Both models are run coupled to the GOTILWA+ model [*Gracia et al.*, 1999; *Keenan et al.*, 2009a], for *Pinus pinea* forests in the Mediterranean Europe region.

seasonal variability can have on estimated monoterpene regional budgets. The scarcity of knowledge on the driving processes behind such seasonal variations leads to large uncertainty when modeling the seasonal cycle of monoterpene emissions. The use of a fixed seasonality relationship with the time of year, as applied in this study, may not be entirely correct due to the probable dependence of seasonality on past light and temperature regimes [*Sharkey and Loreto*, 1993; *Staudt et al.*, 2000], phenology, or water availability [*Bertin and Staudt*, 1996], leading to complex spatiotemporal variations in emission potentials. This is confounded by potential effects of canopy depth on enzyme activity [*Grote*, 2007]. However, considering such affects in a more detailed manner is not possible until a more process-based knowledge of seasonal variations has been gained.

[27] The Niinemets et al. model has a strong relation to light regime and energy production [see *Arneth et al.*, 2007a], as do the MEGAN model algorithms [*Guenther et al.*, 1991, 1993, 1995; *Arneth et al.*, 2007a], which have been widely used, with a fixed emission factor, in regional and global estimates of biogenic VOC emissions inventories [e.g., *Guenther et al.*, 1995; *Levis et al.*, 1999; *Simpson et al.*, 1999; *Wang and Shallcross*, 2000; *Adams et al.*, 2001; *Naik et al.*, 2004; *Parra et al.*, 2004; *Tao and Jain*, 2005; *Lathière et al.*, 2006]. Thus, with a fixed emission factor, emissions can be sustained even in winter because light availability and temperature are still sufficiently high. This is particularly noticeable in the increasing difference in modeled monoterpene emissions at more southern latitudes (Figures 4 and 5), where relatively warm winters led to large monoterpene emissions if the seasonal cycle of emissions potentials is not taken into account. To the best of our knowledge, there is no large scale regional study which takes into account a realistic measure of seasonality.

[28] Species differences in the shape of the E_{M} versus time of year dependencies reflect species-specific differences in phenology as frequently observed in Mediterranean species [e.g., *Pereira et al.*, 1987; *Flexas et al.*, 2001; *Ogaya and Peñuelas*, 2004; *Prieto et al.*, 2009]. The large difference (in the magnitude and timing of emissions) between the response function for *Pinus pinea* and *Quercus ilex* calls into question the validity of applying one empirical parameterization to all species and functional types. Such differences suggest that the empirical introduction of seasonality by the MEGAN model (parameterized with data from five studies of four different species) may not be effective in capturing between species/functional type variations. This has proven to be the case for these two studied species, with both exhibiting markedly different seasonal cycles.

[29] The effect of drought has not been included in this study. Drought has also been shown to greatly reduce summer emissions from forest canopies in the Mediterranean region [*Llusià and Peñuelas*, 1998; *Grote et al.*, 2009; *Lavoir et al.*, 2009]. Various simple reduction functions have been used in modeling studies [*Guenther et al.*, 2006; *Grote et al.*, 2009; *Keenan et al.*, 2009a], though there is no clear understanding as to how to model emission responses to drought [*Grote and Niinemets*, 2008]. A drought-induced reduction in monoterpene emissions during summer would increase the relative importance of the consideration of seasonal variation in the basal emission factor, as spring and autumn emissions (where bigger differences are observed due to seasonality) would have greater weight in the total annual emissions budget. Current understanding of the effect of drought on photosynthesis, and how to model it, has recently improved [*Keenan et al.*, 2009b] but much work is needed to accurately model phenology and interactions between water availability and the timing of phenological responses.

5. Conclusions

[30] We conclude that monoterpene emissions modeled based on midsummer basal emissions factors will inevitably overestimate the annual total and, more importantly, inaccurately predict the annual pattern of emissions. Emission models including seasonality only as light and temperature history are not capable of catching seasonal changes in emission potential. Therefore, the consideration of seasonality is necessary for any regional monoterpene inventory, and a more thorough understanding will likely be crucial for climate change scenario analyses of VOC emissions for many regions. This is particularly true for areas that exhibit drought stress today or in the future and host VOC emitting plants.

[31] The large reduction in the estimated regional emissions due to the inclusion of seasonality, although here specific to monoterpene and the two studied tree species, are expected to be applicable to any tree species and potentially to other biogenic VOCs. This is likely to have large ramifications on regional and global monoterpene emissions estimates, potentially reducing previous emissions inventories by up to 65% in some areas.

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