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Comparing three vegetation monoterpene emission models to measured gas concentrations with a model of meteorology, air chemistry and chemical transport

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Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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BGD

10, 18563–18611, 2013

**Comparing three
monoterpene
emission models**

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Biogenic volatile organic compounds (BVOCs) are essential in atmospheric chemistry because of their chemical reactions that produce and destroy tropospheric ozone, their effects on aerosol formation and growth, and their potential influence on global warming. As one of the important BVOC groups, monoterpenes have been a focus of scientific attention in atmospheric research. Detailed regional measurements and model estimates are needed to study emission potential and the monoterpene budget on a global scale. Since the use of empirical measurements for upscaling is limited by many physical and biological factors such as genetic variation, temperature and light, water availability, seasonal changes, and environmental stresses, comprehensive inventories over larger areas are difficult to obtain. We applied the boundary layer-chemistry-transport model SOSA to investigate Scots pine (*Pinus sylvestris*) monoterpene emissions in a boreal coniferous forest at the SMEAR II site, Southern Finland. SOSA was applied to simulate monoterpene emissions with three different emission modules: the semi-empirical G95, MEGAN 2.04 with improved descriptions of temperature and light responses and including also carbonyl emissions, and a process-based model SIM-BIM. For the first time, the emission models included seasonal and diurnal variations in both quantity and chemical species of emitted monoterpenes, based on parameterizations obtained from field measurements. Results indicate that modelling and observations agreed reasonably well, and that the model can be used for investigating regional air chemistry questions related to monoterpenes. The predominant modelled monoterpene concentrations, α -pinene and Δ^3 -carene, are consistent with observations.

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

The boreal zone is the world's second largest forested region, after tropical forests (Global Forest Resources Assessment, 2000). Boreal vegetation is dominated by evergreen coniferous trees that produce a significant amount of biogenic volatile organic compounds (BVOCs): mainly mono- and sesquiterpenes (Hakola et al., 1998; Rinne et al., 2009). Once emitted from vegetation, BVOCs have potential impacts on global climate due to their effects on atmospheric chemistry, aerosol formation and carbon balance.

BVOCs react with O_3 , OH and NO_3 radicals, and transform to less volatile organic compounds, that in turn condense as secondary organic aerosols (SOA) (Kulmala et al., 2004). They are also crucial for stabilized Criegee radicals (Mauldin et al., 2012). Some of the oxidation products of BVOCs trigger aerosol new particle formation (e.g. Boy et al., 2003; Kanakidou et al., 2005; Kulmala et al., 2013). This affects the optical properties of aerosols (Nozière and Esteve, 2005) and causal feedback mechanisms to the Earth's radiation (Fuentes and Wang, 1999). The oxidation of BVOCs results in the acidity of the precipitation (Kawamura and Usukura, 1993) and the generated carbonyls photolyse and produce free radicals that interact during smog cycles (Tsigaridis and Kanakidou, 2002). Global volatile organic compound (VOC) emissions from biogenic sources (BVOC) have been estimated to be ca. 1000 Tgyr^{-1} (Guenther et al., 2012), and anthropogenic (AVOC) ca. 110 Tgyr^{-1} (Piccot et al., 1992), 149 Tgyr^{-1} (Müller et al., 1992), or 130 Tgyr^{-1} (Lamarque et al., 2010).

As the biogenic sources dominate the atmospheric VOC budget especially in boreal regions, it is important to understand the dynamics of biogenic emissions and their consequences to atmospheric processes. Ecosystem BVOC emissions vary depending on biological (e.g. plant species, plant-specific emission capacity, phenology, biotic and abiotic stresses) and physical factors (e.g. temperature, light and water availability, CO_2 concentration) (e.g. Peñuelas and Staudt, 2010). Many BVOCs are important for plants as defensive compounds, e.g. in preventing the colonization of pathogens after

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



wounding, in deterring insects, or in recruiting the herbivore natural enemies (Visser, 1986; Dicke et al., 1990; Kesselmeier and Staudt, 1999; Tooker et al., 2005).

It is not possible to directly compare modelled BVOC emissions to measured BVOC concentrations in or above the canopy, since these chemicals undergo reactions and mixing in the atmosphere. In this study we include three different emission models to the boundary layer-atmospheric chemistry-transport model SOSA (Model to Simulate the concentrations of Organic vapours and Sulphuric Acid; Boy et al., 2011), and thus simulate the BVOC concentrations at different heights, allowing both chemical reactions and meteorological mixing to have their effect. Model results are compared to observed diurnal and annual in and above canopy monoterpene concentrations measured by proton-transfer-reaction mass spectrometer (PTR-MS). We also analyze the implications for the modelled atmospheric reactivity and monoterpene concentrations when we include (i) variations in emission spectrum and (ii) emissions from soil. The measurements were conducted at the SMEAR II station, Hyytiälä, Southern Finland (Hari and Kulmala, 2005). Since previous research shows that many of the tree species in the European boreal zone are monoterpene emitters (Janson, 1993; Hakola et al., 1998; Hauff et al., 1999), this paper will focus on monoterpene emissions.

2 BVOC emission models

We used three different emission modules for estimating the robustness of atmospheric chemistry and gas concentrations modelled by SOSA: “G95” (Guenther et al., 1995), “MEGAN 2.04” (Model of Emissions of Gases and Aerosols from Nature; Guenther et al., 2006) and “SIM-BIM” (Seasonal Isoprenoid synthase Model – Biochemical Isoprenoid biosynthesis Model; Grote et al., 2006). The emission models coupled with SOSA provide on-line estimates of the landscape-averaged emission rates of monoterpenes and other BVOCs from terrestrial ecosystems into the atmosphere at a specific location and time.

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.1 G95

The emissions of organic vapours from the canopy were calculated as:

$$\text{Emission} = \varepsilon \cdot \gamma \cdot \rho \quad (1)$$

where ε ($\mu\text{g m}^{-2} \text{h}^{-1}$) is an ecosystem dependent emission factor representing the emission of a compound into the canopy at photosynthetically active radiation (PAR) flux of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and leaf temperature of 303.15 K, referred to as standard emission potential. We assumed Scots pine to be the main tree species in our boreal forest ecosystem, and the seasonal standard monoterpene emission potentials used in the model were as given by Tarvainen et al. (2005) and Hakola et al. (2006). γ (normalized ratio) is a non-dimensional adjustment emission factor accounting for emission changes due to deviations from standard conditions, and ρ (normalized ratio) is a factor accounting for production and loss within plant canopies.

The surface emission flux from the vegetation, $F_{\text{vegetation}}$, was calculated in the model as (Guenther et al., 1995):

$$F_{\text{vegetation}} = D_m \cdot \varepsilon \cdot \gamma \quad (2)$$

where D_m ($\text{kg dry matter m}^{-2}$) is the foliar density obtained from the leaf area index (LAI) with 0.538 kg m^{-2} adopted as the constant value at SMEAR II (Ilvesniemi et al., 2009). ε ($\mu\text{g m}^{-2} \text{h}^{-1}$) and γ are the same as above.

2.2 MEGAN 2.04

The improvements in MEGAN 2.04 (Guenther et al., 2006) relative to G95 are that individual VOC species are included in the model and driving variables such as temperature and light in the past days are also accounted for when calculating emissions. Emissions of methanol, formaldehyde, acetone and sesquiterpenes, which may contribute significantly to atmospheric concentrations of VOCs were estimated by MEGAN 2.04

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



but are not part of this study because our third emission module (SIM-BIM, Sect. 2.3) only provide emission rates for monoterpenes. The emission activity factor γ in MEGAN 2.04 is improved, and it accounts for the effects of soil moisture, leaf age and the canopy environment as:

$$\gamma = \gamma_{\text{age}} \cdot \gamma_{\text{SM}} \cdot \gamma_{\text{CE}} \quad (3)$$

where γ_{age} makes adjustments for effects of leaf age. It is calculated with an algorithm that assigns different emission activities to new, growing, mature, and old leaves. γ_{SM} accounts for direct changes in γ due to changes in soil moisture. γ_{CE} describes variation due to LAI and light, temperature, humidity and wind conditions within the canopy environment and is estimated as:

$$\gamma_{\text{CE}} = C_{\text{CE}} \cdot \gamma_{\text{PT}} \cdot \text{LAI} \quad (4)$$

where C_{CE} is a factor that sets the emission activity to unity at standard conditions, γ_{PT} is the weighted average of the product of a temperature emission activity factor (γ_{T}) and a photosynthetic photon flux density (PPFD) emission activity factor (γ_{P}), LAI is the leaf area index. MEGAN 2.04 extends algorithms for estimating γ_{T} and γ_{P} instead of using the constant values recommended by Guenther et al. (1999), which improves the simulated variations in emission associated with past temperature and PPFD conditions (Guenther et al., 2006). Previous studies show that measured terpenoid standard emission potentials are higher when warm sunny conditions have occurred during the previous days and are lower if there were cool shady conditions (Sharkey et al., 2000). The impact on vegetation emissions by exposure to different temperature and light could last for several weeks (Pétron et al., 2001). The factors controlling these variations may operate over a continuous range of time scales, but for modelling purposes, MEGAN 2.04 considers only 24 h and 240 h (Guenther et al., 2006).

MEGAN 2.04 uses canopy scale emission factors, which differs from most other biogenic emission models which use leaf scale emission factors. Although canopy scale measurements are becoming more available, the MEGAN 2.04 canopy scale emission

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



MEP with the presence of NADPH which is considered a constant in the model. MEP reacts further to IDP. IDP and DMADP are both 5 carbon atoms and in equilibrium, with a certain equilibrium constant. When IDP and DMADP build together to form the 10 carbon monoterpene backbone molecule GDP, a monoterpene is emitted. The potential production rates are determined by activities of isoprenoid biosynthesis related enzymes (Grote et al., 2010).

The formulation of the SIM-BIM emission model used here follows the original isoprene emission model by Zimmer et al. (2000) with monoterpene emissions as added by Grote et al. (2006) linked to a photosynthesis model by Noe and Giersch (2004). However, the model variables and parameters were scaled to be applicable at the level of the gas exchange surfaces of trees. This includes some modifications to the model. All pools are rates per area and not concentrations as typical for enzymatic reaction systems. Due to lack of validation data for conifers with several actively emitting needle ages, the seasonal changes modulating the reaction velocities in the seasonality module (Lehning et al., 2001, parameterized for deciduous oak trees) have not been applied. Instead, we parameterised the model equations with shoot chamber measurements data from year 2007. Sets of two continuous days were picked out of each season (spring, summer, autumn and winter) of the 2007 data. We defined a distance function and the minimization criteria was to minimize the root mean square difference between the model and measured data. Each parameter was allowed to change within a certain interval and for each set of picked data, 30 000 random choices of the parameters were realised using a normal distribution and tested against the criteria. Parameter combinations that successfully minimized the criterion were then chosen.

The model equations and parameter values of SIM-BIM as used in this study are presented in Appendix A.

2.4 Chemotype effect on emissions

Recent research carried out e.g. at the field station SMEAR II (Bäck et al., 2012) has demonstrated that the Scots pine individuals differ on their chemotypes, i.e. inherited

capability of the tree individual to emit monoterpenes of a specific blend. Emissions can be dominated by either pinenes (both α -pinene and β -pinene), Δ^3 -carene or a tree can have an intermediate chemotype and emit both in almost equal quantities. Table 1 shows the different monoterpene emission distributions from 40 sampled trees at the SMEAR II stand (data from Bäck et al., 2012). SOSA (see below) was employed to test the effects of chemodiversity on modelled monoterpene concentrations, OH reactivity and OH concentrations. Chemotype distribution according to Table 1 was set up into the model, so for different model runs we assumed all the trees were either of pinene type, carene type, intermediate type, or of a type described by the average of the population.

3 Meteorology and chemistry models

SOSA (Boy et al., 2011; Mogensen et al., 2011) is a one-dimensional boundary layer and chemistry transport model. SOSA predicts wind, temperature, humidity, turbulence kinetic energy, dissipation and turbulent eddy diffusivity, and the corresponding fluxes, for each height level. We used 51 height levels in the model, with increasing thickness for the higher levels. The levels start from ca. 20 cm thickness near the ground, have ca. 3 m thickness above the canopy (18 levels inside the canopy), up to 250 m thickness at the model top at 3 km height. The following inputs were used for running SOSA: vertical leaf area density and canopy physiological parameters for the SMEAR II site. Meteorological data from nearby meteorological observations (Jokioinen and Tikkakoski sounding stations) were used as model top (3000 m height) boundary conditions. Continuously measured meteorological data (temperature, humidity and wind speed at 4, 8, 16, 33, 50 and 67 m heights) from the SMEAR II mast were used for nudging the model variables towards the observations. The measured incoming solar radiation at SMEAR II was used for photochemistry, photosynthesis and energy balance.

The chemical kinetics module simulates the time evolution of the concentrations of the chemical species and reactions occurring at different levels in the atmosphere. The chemical reaction equations and the corresponding rate coefficients for

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the model were selected from the Master Chemical Mechanism (MCM version 3.1; <http://mcm.leeds.ac.uk/MCM/>). 2140 reaction equations and 761 chemical species were used. These reactions represent the complete reaction paths for isoprene, β -pinene, α -pinene, 2-methyl-3-buten-2-ol, methanol, methane, acetone, acetaldehyde, formaldehyde and all relevant inorganic reactions. As the MCM version 3.1 only included full chemistry pathways for the terpenes α -pinene and β -pinene, we adopted rate constants from Atkinson et al. (1994) for Δ^3 -carene, limonene, sabinene and camphene with OH, O₃ and NO₃. For other monoterpenes we used the reaction rates of α -pinene for the first reactions.

The Kinetic PreProcessor (KPP) (Damian, 2002; Sandu and Sanders, 2006) was used to translate the MCM reaction equation into Fortran code to code that performs the time integration of the kinetic system, and functions as a module to SOSA. Numerical solution of the system of these 761 differential equations, and for each 51 height levels, was the part that used most computer resources. SOSA is written as a parallel program, and simulating e.g. one month, with 10 s time step in the model, took ca. one hour when ran using 32 processor cores on a Linux cluster.

For a more detailed description of the model SOSA we refer to Boy et al. (2011) and Mogensen et al. (2011).

4 Measurements

4.1 The SMEAR II site

The study was carried out at the SMEAR II (Station for Measuring forest Ecosystem–Atmosphere Relations, 61°51' N, 24°17' E, 180 m a.s.l.) located in the vicinity of the Hyytiälä Forestry Field Station in Southern Finland. This is a unique field measurement station designed for continuous measurements of phenomena in which physical, chemical and biological processes interact (Hari and Kulmala, 2005). Vegetation at the station is dominated by 50 yr old Scots pine (> 60%), and the rest are Norway

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



spruce (*Picea abies* (L) Karst.), European aspen (*Populus tremula* L.) and birch (*Betula pendula* Roth.) (Aaltonen et al., 2011). The average tree density is approximately 1370 stems (diameter-at-breast height > 5 cm) per hectare and the stand height is about 16 m with the open canopy (Ilvesniemi et al., 2009). Vascular plant species at the ground level are mainly lingonberry (*Vaccinium vitis-idaea* L.), bilberry (*Vaccinium myrtillus* L.), wavy hair-grass (*Deschampsia flexuosa* (L.) Trin.) and heather (*Calluna vulgaris* (L.) Hull.), while the most common mosses are Schreber's big stem moss (*Pleurozium schreberi* (Brid.) Mitt.) and a dicranum moss (*Dicranum* Hedw. sp.) (Ilvesniemi et al., 2009). The soil at the stand is mainly podzolic, characterized by thin humus layer and low nitrogen level. The 30 yr average annual precipitation at SMEAR II is 711 mm and annual mean temperature is 3.5 °C (Pirinen et al., 2012). More detailed information of the station can be found under <http://www.atm.helsinki.fi/SMEAR> or Vesala et al. (1998) and Kulmala et al. (2001).

4.2 VOC concentration and emission measurements

VOC concentrations were measured with a PTR-MS (Proton-Transfer-Reaction Mass Spectrometer, Ionicon Analytik, Innsbruck, Austria). In the PTR-MS compounds are ionized with a proton and detected at their protonated molecular mass ($M+1$), and thus all monoterpenes were detected as a sum at $M137$ (amu per charge). The monoterpenes were calibrated with an α -pinene standard every second week and background measurements of VOC free air were done every second or third hour. The sampling, calibration and concentration calculation protocol is described in detail by Taipale et al. (2008). Monoterpene concentrations were measured from continuous sampling flows from above canopy (22 m height), top part of the canopy (16 m) and from the below-canopy space (4 m).

4.3 Forest floor emissions

VOC emissions from soil and ground vegetation were measured using three flow-through chambers between January to June 2009. The chambers (80 cm × 40 cm × 25 cm) coated with a transparent fluorinated ethylene-propylene film were mounted on the permanently installed collars. The operation of the chambers was automated; each chamber was pneumatically closed for 15 min once every three hours, i.e. eight times per day, and the first 7 min non-steady-state part of the closures was used for quantifying the fluxes. Sample air was drawn from the chambers at a rate of 1.1 dm³ min⁻¹ and a smaller air sample (flow 0.1 dm³ min⁻¹) was diverted into PTR-MS with polytetrafluoroethylene tubing. Compressed ambient air was supplied into the chamber at the same flow rate as the sample air was drawn out to replace the sampled air volume in the chamber. VOC fluxes were calculated by fitting the mass balance equation to the development of measured VOC concentrations during chamber closure. The measurement setup and flux calculations are described in detail by Aaltonen et al. (2013).

The measured calibrated emission of protonated mass 137 with PTR-MS was read into the SOSA model in order to test the effect on the ambient monoterpene concentration from forest floor monoterpene emissions. An average was taken of the data from the three cuvettes, since these showed different fluxes, which is mostly due to the heterogeneity of soil and vegetation inside the cuvettes. The total monoterpene flux signal was divided into individual monoterpenes according to the average chemotype tree distribution given by Bäck et al. (2012) (as also seen in Table 1), since previous studies indicated that surface needle litter (Steinbrecher et al., 1999; Aaltonen et al., 2011; Hayward et al., 2001) contribute to the forest floor monoterpene emissions. We then linearly interpolated the measured flux of monoterpenes from the soil to fit our model time step and multiply with the height of our lowest layer (= 17 cm) and our chemistry module time step, and added this concentration to the already existing monoterpene concentration in the lowest model layer. Due to mixing, the soil emitted monoterpenes will then disperse to higher vertical levels. If the measured flux was negative (due to

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measurement uncertainties and potentially also deposition to humid surfaces), we set the soil emission to zero.

5 Results and discussion

In this section we validate the performance of the model with different chemotypic pine trees at SMEAR II and then compare the simulated results of monoterpenes with available measurements. Further, the seasonal, diurnal and vertical distributions of monoterpene concentrations are analyzed and the model uncertainties are discussed at the end.

5.1 Tree chemotype effects on canopy air chemistry

Table 2 shows the monthly mean concentrations for the sum of monoterpenes at 14 m height for three chemotype scenarios, and for the scenario of average over chemotypes, when run with the MEGAN 2.04 emission model. As expected, relatively large differences in the total monoterpene concentrations in the air are found between pinene type and carene type stands. This can be explained by atmospheric chemistry of these compounds. Monoterpenes mainly react with hydroxyl radical (OH) during daytime and nitrate radical (NO_3) during nighttime. However, Δ^3 -carene has higher reaction rates with both of these radicals ($88 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) than α -pinene ($53.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $6.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Hakola, 2002). Therefore, more of α -pinene emitted from different levels of the canopy can be transported to the 14 m measurement height before it has undergone reactions. Since the ozone concentrations at SMEAR II are small and monoterpene reaction rates with ozone are rather low, the impact from ozone is minor. The intermediate emission chemotype results are between the two other groups and quite similar to the average scenario.

BGD

10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The hydroxyl radical is the most important oxidant in the troposphere, and the level of its sources and sinks are considered as the criterion when evaluating the oxidation capacity of the atmosphere. OH reactivity is defined as the total loss rate of OH radicals from the atmosphere and calculated by the sum of concentration of the reactants in OH-reactions multiplied by the specific reaction rates (similar to as calculated by Mogensen et al., 2011). The differences in modelled diurnal profiles of OH reactivity between the three chemotypes are most clear at the nighttime and early morning hours, with differences up to a factor of 1.5 between the pinene scenario and the carene scenario (Fig. 2). This is due to the higher monoterpene concentrations remaining in the atmosphere in the pinene chemotype scenario than in the carene chemotype scenario, after consumption by the nitrate radical. During daytime, relatively low monoterpene concentrations in the ambient air are available to react with the abundant OH radicals, so at daytime the chemotype scenarios do not differ in OH-reactivity.

The differences in diurnal profiles of OH concentrations between the chemotype scenarios are small (Fig. 3). Although the monoterpene concentrations in the pinene scenario are higher during daytime, they have lower reaction rates with OH radicals. These opposite effects result in an OH concentration of only about 5% lower in the pinene scenario, compared to the carene scenario.

Since different monoterpenes have significantly different aerosol yields, they should have different potentials in new particle formation and growth. Ignoring tree chemodiversity may cause bias in related modelling results. The results from model simulations (Table 2, Figs. 2 and 3) demonstrate the magnitude of potential biases in air chemistry modelling, if a model is based on only a single tree chemotype.

5.2 Comparing different models with measurements

For emission model intercomparison, we used the averaged chemotype scenario (see previous section). All models reproduce the annual pattern of monthly averages fairly well, especially during the highest concentrations in the summer (Fig. 4). In August–September, G95 and MEGAN 2.04 underestimate notably more than SIM-BIM, and

in October–December all models overestimates the concentrations. The spring (April–May) high concentrations are best predicted by the SIM-BIM, whereas the MEGAN versions underestimate the concentrations by about 30 %.

In all three models, daytime emissions are around two times higher than those at night (Fig. 5), which corresponds to the reported daily pattern of emissions (e.g. Tarvainen et al., 2005). Otherwise all of the models agree quite well but in summer, SIM-BIM produces higher daytime emissions than G95 and MEGAN 2.04. Grote et al. (2006) have discussed that SIM-BIM might overestimate emissions during the hottest season, potentially due to lower enzyme activities during drought periods. The estimation of emission amounts has uncertainties related to measurements, model structure, and model parameters (Grote et al., 2010).

With respect to these different emission models, it is not possible to judge which one is best: all of them offer sensible simulation results. Nevertheless, we have chosen to proceed using MEGAN 2.04 and compare the model results with the measured concentrations and fluxes at the SMEAR II site (Figs. 6 and 7). The simulations yield a fairly good fit to measurements at both below and above canopy. The concentration minima appear at midday and the maxima at midnight, meaning that monoterpenes would be accumulated during the night since emissions are not zero at night, but continue in the absence of sunlight from the constitutive storage pools of needles and trunks (e.g. Schuh et al., 1997; Loreto et al., 2000; Niinemets et al., 2002b; Schurgers et al., 2009). Although the total emissions are much higher during daytime, increased turbulent mixing and chemical reactions with hydroxyl radicals consuming a large amount of monoterpenes result in the lowest concentrations during day. The daytime contribution of the endogenous storage pools to monoterpene emissions from Scots pine can be about 40 % (Ghirardo et al., 2010), whereas at night, emissions from permanent storage make up most of the detected monoterpenes and are based on exponential temperature dependency. The storage pool size in conifer tissues is dependent on the turnover rate of stored compounds, which is in turn a product of filling up the storage by de novo synthesis and of the temperature dependent evaporation from storage

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(Shurgers et al., 2009). It is evident that the long-term storage dynamics is an important feature that should be implemented in models in future, and that the emissions from storage may also influence concentrations of some compounds (Sallas et al., 2003; Ghirardo et al., 2010).

5.3 Monoterpene emissions from forest floor

Understanding of processes related to monoterpene emissions from soil, ground vegetation and decomposing litter is still limited but their role in ecosystem scale emissions is not negligible. During high forest floor emission seasons like spring and autumn, the emissions from soil and ground vegetation can be ca. 10% of the total monoterpene emissions from the forest ecosystem at SMEAR II (Aaltonen et al., 2011, 2013). Previous studies have indicated that both surface needle litter (Steinbrecher et al., 1999), soil microorganisms (Bäck et al., 2010) and roots (Janson, 1993) contribute to monoterpene emissions (Hayward et al., 2001). Greenberg et al. (2012) used enclosure and micrometeorological techniques to quantify a small (< 1%) contribution of litter and roots to the ecosystem scale monoterpene flux in a temperate pine forest. The variation of emissions from forest floor throughout the year is suggested to originate from changes in litter quantity and quality, soil microbial activity and the physiological stages of plants (Aaltonen et al., 2011). In autumn when the oldest age class of needles drop to the floor, the stored monoterpenes from the litter will be released during decomposition (Aaltonen et al., 2011), which makes the emissions even higher than during summer, although weather conditions in autumn are less favourable. Emissions from ground vegetation and soil can even be sustained throughout the year, as shown by high concentrations inside the snowpack (Aaltonen et al., 2012).

Measured forest floor emission of monoterpenes (Aaltonen et al., 2013) were read into the model in order to test the effect of forest floor processes on the ambient monoterpene concentrations. During winter (January and February) when the soil is cold and covered by snow, the soil flux is low and therefore the contribution to the total monoterpene flux is negligible, which is why we observe a very small increase in near-

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ground monoterpene concentration. An obvious increase (around 10%) of monoterpene concentrations caused by soil emissions is visible especially in spring and late spring when the soil is active (Fig. 8). However, especially in April the model was not able to capture this dynamics properly and we observe a large underestimation compared with the measured concentration. Autumn is usually supposed to be the other peak season, but at this time, data were not available for autumn, and therefore the model was only run for springtime. The dynamic processes of monoterpene emissions from forest floor are still poorly understood and more field data are needed to explain the controlling mechanisms.

5.4 Monoterpene composition at SMEAR II

As different monoterpenes differ in their atmospheric lifetime and reactivity, it is important to identify the monoterpene composition in the ambient air. According to simulations (with MEGAN 2.04), the most abundant monoterpenes were α -pinene and Δ^3 -carene (Fig. 9). This is compatible with the measured data as well as with many other studies (Rinne et al., 1999; Hakola et al., 2006; Tarvainen et al., 2007). β -pinene also contributes significantly to the total monoterpene concentration, 18% according to the model, 5% in observations. These three compounds represented over 90% of the total monoterpene concentration in both modelling or and measurements.

Camphene, sabinene and limonene contributed, in decreasing order, to model results, with a proportion of 10% in total, but much less in the measurements, except limonene slightly more. The other species could be 1,8-cineole, ocimene or maybe some other monoterpenes with small concentrations but high reactivity in the atmosphere.

The composition distributions of modelling and observations were somehow different: β -pinene and camphene were more abundant whereas Δ^3 -carene was less abundant in the simulations compared with the measured values. The reason could be explained by the chemistry of monoterpenes in the troposphere. As mentioned before, Δ^3 -carene ($9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) has a much faster reaction rate to react

with nitrate radical at night than β -pinene ($2.51 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and camphene ($6.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In Fig. 9, the modelled composition was the average of both day and night monoterpene concentrations, but the measured one was the daytime distribution from the study by Hakola et al. (2009). At nighttime, Δ^3 -carene was consumed to a large extent, however, β -pinene and camphene were accumulated. Therefore, Δ^3 -carene was 40 % in the measured composition, but dropped to 23 % in the modelled, while the ratios of β -pinene and camphene in the simulations were doubled and tripled, respectively.

5.5 Seasonal and diurnal variation in monoterpene concentrations

According to many previous studies, the seasonal differences in monoterpene emissions cannot be reconciled solely with instantaneous meteorological data of light and temperature. Increasing evidence shows that a great part of seasonal variations in emissions results from long term plant phenological responses, such as budding, flowering, fruiting, defence-related metabolism, leaf senescence, and dormancy (Robertson et al., 1995; Hakola et al., 1998; Niinemets et al., 2002a; Lappalainen et al., 2009; Monson et al., 2012). Growth conditions like past and current temperature, light intensity, nutrition status, and water availability are linked to the variations as well (Sharkey and Loreto, 1993; Bertin and Staudt, 1996; Serca et al., 2001).

Table 3 summarizes the modelled relative contributions of individual monoterpenes to concentrations at the top of the canopy in different seasons. The spectrum is quite similar throughout the whole year, with the largest contributor being α -pinene, followed by Δ^3 -carene and β -pinene. This is consistent with observations (Hakola et al., 2009) at the SMEAR II site, and also with findings from a Scots pine forest in southern Germany (Komenda and Koppmann, 2002). The three main compounds accounted for ca. 90 % throughout the year. Almost 50 % of monoterpenes was α -pinene in all seasons, and Δ^3 -carene was slightly higher in spring and summer, but lower in autumn and winter than β -pinene. Camphene, sabinene and limonene were minor constituents of the total

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



monoterpene concentrations and other uncertain monoterpenes accounted for about 1 % from the total.

The concentrations reach the maximum in June–August due to strong biogenic emissions in summer (Fig. 10) (Hakola et al., 2006, 2009). A clear seasonal cycle is visible with higher concentrations in early spring and then a decrease in late spring. This type of seasonal behaviour was also described by Tarvainen et al. (2005), Hakola et al. (2006) and Lappalainen et al. (2009). Potential reasons for high springtime emissions are the storage pool dynamics, stresses during the spring recovery period and physiological factors related to breaking of dormancy. Tarvainen et al. (2005) and Schurgers et al. (2009) have proposed that the storage pools of monoterpenes might be empty after winter, and the new emissions first occur with the light dependent production (strong irradiance in connection with rather low temperature and low water availability in early spring).

5.6 Vertical profiles of monoterpene concentrations

The modelled and measured daily vertical distribution of monoterpene concentrations in summer and winter presented in Figs. 11 and 12 give qualitative insights into monoterpene sources and sinks in this forest canopy. The higher concentrations inside the canopy at night demonstrate that emissions originate mainly from the forest canopy. Consistently, very low values, both in summer and in winter, were always found near the ground. The concentrations at all heights were about 3–4 times higher in summer than in winter, indicating stronger emissions in summer. The daytime convective mixed layer concentrations are controlled by a balance between emissions from vegetation and reaction with OH, the main daytime sink (Kuhn et al., 2002). Despite high emissions, turbulent mixing and reactions with OH reduced the concentrations. Turbulent mixing due to thermal convection as the day progresses made monoterpenes well mixed at all height levels in the atmospheric boundary layer during the day in summer, whereas the turbulence and mixing were slower during winter, which results in weaker transport of monoterpenes at winter daytime. High nighttime concentrations in the two figures are

18582

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10, 18563–18611, 2013

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



evident, indicating that monoterpene concentrations were quite stable at night without the influence of photochemistry and vertical mixing. High nighttime concentrations also supports the theory of continuous monoterpene emissions at night from Scots pine storage pools.

5 Modelled vertical profile of monoterpene concentrations agreed reasonably well with the observations. The best correspondence is found near canopy top at nighttime in both summer and winter. The contours in modelled vertical profile are more detailed, since measured monoterpene concentrations were conducted only at three heights (4 m, 14 m, 22 m). Observed monoterpene concentrations were at the same order of
10 magnitude with the simulations both in summer and in winter and appeared in similar distribution patterns as described above. This demonstrates that SOSA is able to reproduce meaningful profiles at least for the nighttime monoterpene concentrations.

5.7 Model uncertainties

15 Despite the progress in understanding biogenic emissions from vegetation, uncertainties in emission estimates are still large due to several reasons (e.g. Arneth et al., 2008). Based on comparisons with above canopy measurements, an uncertainty factor of 3 for monoterpene emissions has been reported in German regions where accurate model inputs are available (Smiatek and Steinbrecher, 2006). Stewart et al. (2003) reported an uncertainty factor of 4 for biogenic emissions in Great Britain, and Simpson et al. (1999) an uncertainty factor of 3 to 5 for isoprene and monoterpene emissions from vegetation in European scale. Specific to our research, the uncertainties in
20 monoterpene estimates result from insufficient knowledge on the canopy scale emission potentials and on the mechanisms controlling emissions, related to variations in plant physiological activity.

25 The Scots pine emission algorithms used in SOSA were only used for monoterpenes, and thus are not representing isoprene emission at the SMEAR II stand. The stand is pine dominated, but some isoprene is emitted by the co-occurring species such as Norway spruce, European aspen and many willow species. Further, the large,

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



inherited chemotypic variations in emission spectrum between individuals of the same tree species are indicating the problems in obtaining emission parameters from too few individuals. The emission spectrum averaged from several tree individuals may be the best way to obtain robust emission parameters.

6 Conclusions

We described three monoterpene emission models (G97, MEGAN, SIM-BIM) and used these, together with the chemistry-transport model SOSA, to model monoterpene concentrations in the air at different heights in canopy, and compared the simulations to the measured concentrations and atmospheric OH-reactivity over the year in a boreal pine forest stand. All three models agreed fairly well with the measurements upon the seasonal emission patterns (especially in the midsummer period), although the theoretical basis of the models was quite different. The modeled (MEGAN) monoterpene and OH concentrations seem to be very sensitive to variations in emission composition, which can lead to about 30 % bias in atmospheric OH-reactivity estimates. Implementing the ground vegetation and soil as a source for monoterpenes seems to be necessary since they may account for about 10 % of the total stand emissions at times, but more process-based understanding is required.

Based on this model comparison, we believe that it is feasible to improve atmospheric chemistry models so that the seasonal and diurnal emission variability is captured in a sufficient way, although there is insufficient knowledge related to other sources than the canopy, plant species and chemotype specific emission potentials and processes regulating the emissions in the transient spring and autumn periods.

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Appendix A

SIM-BIM emission model equations and parameters

Photosynthesis model equations:

$$\frac{d}{dt}g_s = k_g \left(G_{\max} \min \left(\frac{\alpha I}{\beta + I}, \min \left(1 - \frac{VPD}{VPD_0}, 1 \right) \right) \right) - g_s \quad (A1)$$

$$5 \quad \frac{d}{dt}C_i = g_s(C_a - C_i) - \frac{\phi v_l I}{k_l + I} C_i \quad (A2)$$

$$\frac{d}{dt}A_{ps} = \frac{\phi v_l I}{k_l + I} C_i - \theta A_{ps} - R_d \quad (A3)$$

BVOC emission model equations:

$$\frac{d}{dt}GAP = \frac{(1 - f_{PGA})(A_{ps}/3 + R_d)^2}{k_{MTP} + A_{ps}/3 + R_d} - V_{DXP} \frac{GAP}{K_{DXP,GAP} + GAP} \frac{PGA}{K_{DXP,PGA} + PGA} \quad (A4)$$

$$10 \quad \frac{d}{dt}PGA = \frac{f_{PGA}(A_{ps}/3 + R_d)^2}{k_{MTP} + A_{ps}/3 + R_d} - V_{DXP} \frac{GAP}{K_{DXP,GAP} + GAP} \frac{PGA}{K_{DXP,PGA} + PGA} \quad (A5)$$

$$\frac{d}{dt}NADPH = 0 \quad (A6)$$

$$\frac{d}{dt}DXP = V_{DXP} \frac{GAP}{K_{DXP,GAP} + GAP} \frac{PGA}{K_{DXP,PGA} + PGA} - V_{MEP} \frac{NADPH DXP}{K_{MEP,DXP} DXP + K_{MEP,NADPH} NADPH + NADPH DXP} \quad (A7)$$

$$\frac{d}{dt} \text{MEP} = V_{\text{MEP}} \frac{\text{NADPH DXP}}{K_{\text{MEP,DXP}} \text{DXP} + K_{\text{MEP,NADPH}} \text{NADPH} + \text{NADPH DXP}} - V_{\text{IDPs}} \frac{\text{MEP}}{K_{\text{IDPs}} + \text{MEP}} \quad (\text{A8})$$

$$\frac{d}{dt} \text{IDP} = V_{\text{IDPs}} \frac{\text{MEP}}{K_{\text{IDPs}} + \text{MEP}} - V_{\text{IDPi}} \frac{\left(\text{IDP} - \frac{\text{DMADP}}{K_{\text{eq,IDPi}}}\right)}{K_{\text{IDPi,IDP}} \left(1 + \frac{\text{DMADP}}{K_{\text{IDPi,DMADP}}}\right) + \text{IDP}} - V_{\text{GDPS}} \frac{\text{DMADP}}{K_{\text{GDP,DMADP}} + \text{DMADP}} \frac{\text{IDP}}{K_{\text{GDP,IDP}} + \text{IDP}} \quad (\text{A9})$$

$$\frac{d}{dt} \text{DMADP} = V_{\text{IDPi}} \frac{\left(\text{IDP} - \frac{\text{DMADP}}{K_{\text{eq,IDPi}}}\right)}{K_{\text{IDPi,IDP}} \left(1 + \frac{\text{DMADP}}{K_{\text{IDPi,DMADP}}}\right) + \text{IDP}} - V_{\text{Is}} \frac{\text{DMADP}}{K_{\text{Is}} + \text{DMADP}} - V_{\text{GDPS}} \frac{\text{DMADP}}{K_{\text{GDP,DMADP}} + \text{DMADP}} \frac{\text{IDP}}{K_{\text{GDP,IDP}} + \text{IDP}} \quad (\text{A10})$$

$$\frac{d}{dt} \text{Isoprene} = V_{\text{IDPi}} \frac{\left(\text{IDP} - \frac{\text{DMADP}}{K_{\text{eq,IDPi}}}\right)}{K_{\text{IDPi,IDP}} \left(1 + \frac{\text{DMADP}}{K_{\text{IDPi,DMADP}}}\right) + \text{IDP}} - d_{\text{Isoprene}} \text{Isoprene} \quad (\text{A11})$$

$$\frac{d}{dt} \text{GDP} = V_{\text{GDPS}} \frac{\text{DMADP}}{K_{\text{GDP,DMADP}} + \text{DMADP}} \frac{\text{IDP}}{K_{\text{GDP,IDP}} + \text{IDP}} - V_{\text{MTs}} \frac{\text{GDP}}{K_{\text{MTs}} + \text{GDP}} - V_{\text{GGDPS}} \left(\frac{\text{GDP}}{K_{\text{GGDPS}} + \text{GDP}}\right)^2 \quad (\text{A12})$$

$$\frac{d}{dt} \text{Mono} = V_{\text{MTs}} \frac{\text{GDP}}{K_{\text{MTs}} + \text{GDP}} - d_{\text{Mono}} \text{Mono} \quad (\text{A13})$$

Note: The isoprene rate (Eq. 11) was not used in this study, and the Scots pines dominating the stand are monoterpenes emitters.

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Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Comparing three
monoterpene
emission models**

S. Smolander et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Comparing three monoterpene emission models

S. Smolander et al.

Table 1. Average proportions of monoterpenes from emission in the dataset by Bäck et al. (2012) from three different tree chemotypes, and the average of the whole dataset.

	Pinene trees (<i>n</i> = 15) mean	Intermediate trees (<i>n</i> = 17) mean	Δ^3 -carene trees (<i>n</i> = 8) mean	Average of all trees (<i>n</i> = 40) mean
α -pinene	0.601	0.420	0.169	0.437
Δ^3 -carene	0.144	0.445	0.764	0.396
β -pinene	0.171	0.053	0.018	0.090
limonene	0.037	0.019	0.003	0.023
camphene	0.018	0.022	0.008	0.018
terpinolene	0.003	0.008	0.020	0.009
p-cymene	0.001	0.001	0.001	0.001
1,8-cineol	< 0.0005	0.001	0.001	0.001

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Comparing three monoterpene emission models

S. Smolander et al.

Table 2. Modelled (MEGAN 2.04) monthly mean monoterpene concentrations at 14 m for the year 2007, for four different scenarios assuming that the pine trees are of either (i) pinene, (ii) carene, (iii) intermediate chemotype, or (iv) average of all three types. For the scenarios, see Table 1. (Numbers in: 10^9 molecules cm^{-3}).

Scenario	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Pinene	1.60	1.01	2.87	1.52	3.37	8.30	11.0	4.76	1.50	3.22	1.38	1.45
Carene	0.73	0.54	1.66	0.91	1.99	5.69	7.11	3.20	0.79	1.47	0.61	0.61
Intermediate	1.08	0.72	2.11	1.15	2.53	6.59	8.59	3.76	1.08	2.18	0.92	0.95
Average	1.20	0.79	2.30	1.24	2.74	7.05	9.20	4.02	1.18	2.42	1.03	1.06

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Comparing three monoterpene emission models

S. Smolander et al.

Table 3. Modelled (MEGAN 2.04) seasonal contributions of individual monoterpene proportions (in % to total monoterpene concentrations) at 14 m height for year 2007 at each season.

Monoterpenes (%)	Spring	Summer	Autumn	Winter
α -pinene	48.76	47.16	51.99	49.59
Δ^3 -carene	21.67	23.57	16.03	13.46
β -pinene	18.85	17.45	20.76	22.14
Camphene	5.87	5.96	6.64	10.38
Sabinene	2.18	3.17	2.09	2.32
Limonene	1.18	1.07	1.37	1.31
Others	1.35	1.66	1.33	0.80

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table A1. SIM-BIM photosynthesis model variables, and constants with values.

State variables			
g_s		$\text{mmol m}^{-2} \text{min}^{-1}$	stomatal conductance
C_i		ppm	leaf internal CO_2 concentration
A_{ps}		$\mu\text{mol m}^{-2} \text{min}^{-1}$	assimilation by photosynthesis
Input variables			
I		$\mu\text{mol photons m}^{-2} \text{s}^{-1}$	PAR (Photosynthetically Active Radiation)
VPD		kPa	vapour pressure deficit
Constants			
k_g	0.11	min^{-1}	stomatal conductance rate constant
G_{max}	61	mmol m^{-2}	max. stomatal opening
α	1.2	(unitless)	slope of stomatal opening according to light
β	133.6271	$\mu\text{mol photons m}^{-2} \text{s}^{-1}$	curvature of stomatal opening according to light
VPD_0	3	kPa	max. vapour pressure deficit
C_a	380	ppm	air ambient CO_2 concentration
ϕ	0.00185	(unitless)	empirical scaling of C_i to the whole shoot ^a
v_j	6.5	$\mu\text{mol m}^{-2} \text{min}^{-1}$	max. speed of assimilation
k_j	463.13	$\mu\text{mol m}^{-2}$	kinetic constant for assimilation
θ	0.6	min^{-1}	usage of assimilates ^b
R_d	0.2	$\mu\text{mol m}^{-2} \text{min}^{-1}$	respiration

^a The photosynthetic assimilation process takes place inside the chloroplasts and therefore, the process of using leaf internal CO_2 concentration need to be scaled such as it would take place on the gas exchanging area of a coniferous shoot.

^b The Calvin cycle intermediates feed back on the carboxylation rate and a fraction of the fresh assimilated C3 bodies are not instantly available (see Noe and Giersch, 2004).

Table A2. SIM-BIM BVOC emission model variables and constants with values.

State variables		
GAP	mol m^{-2}	glyceraldehyde-3-phosphate
PGA	mol m^{-2}	3-phosphoglyceric acid
NAPDH	mol m^{-2}	reduced form of nicotinamide adenine dinucleotide phosphate
DXP	mol m^{-2}	1-deoxy-D-xylulose 5-phosphate
MEP	mol m^{-2}	2-C-methyl-D-erythritol 4-phosphate (methylerythritol phosphate)
IDP	mol m^{-2}	isopentenyl diphosphate
DMADP	mol m^{-2}	dimethylallyl diphosphate
Isoprene	mol m^{-2}	isoprene
GDP	mol m^{-2}	geranyl diphosphate
Mono	mol m^{-2}	monoterpenes
Constants		
V_Y	$\text{mol m}^{-2} \text{min}^{-1}$	In general, max. rate of reaction producing Y
$K_{Y,X}$	mol m^{-2}	In general, Michaelis constant for reaction $X \rightarrow Y$ (concentration at which rate is half of max. rate)
V_{DXP}	1.9	
$K_{\text{DXP,GAP}}$	6.16	
$K_{\text{DXP,PGA}}$	6.16	
V_{MEP}	8.22	
$K_{\text{MEP,DXP}}$	3.73333	
$K_{\text{MEP,NADPH}}$	9.3333	
V_{IDPs}	6.34	
K_{IDPs}	7.84	
V_{IDPI}	1.9467	
$K_{\text{IDPI,IDP}}$	1.30667	
$K_{\text{IDPI,DMADP}}$	1.30667	
$K_{\text{eq,IDPI}}$	5.78667	
V_{GDPs}	81.57	
$K_{\text{GDP,DMADP}}$	1.58667	
$K_{\text{GDP,IDP}}$	1.04533	
V_{is}	9.893	
K_{is}	9.33333	
V_{MTs}	0.9893	
K_{MTs}	9.3333	
V_{GGDPs}	8.157	
K_{GGDPs}	1.58667	
K_{MTP}	80	
d_{isoprene}	0.0085 min^{-1}	isoprene diffusion rate
d_{Mono}	0.0016 min^{-1}	monoterpenes diffusion rate
f_{PGA}	0.335 (unitless)	fraction of PGA drainage for the assimilate

Comparing three monoterpene emission models

S. Smolander et al.

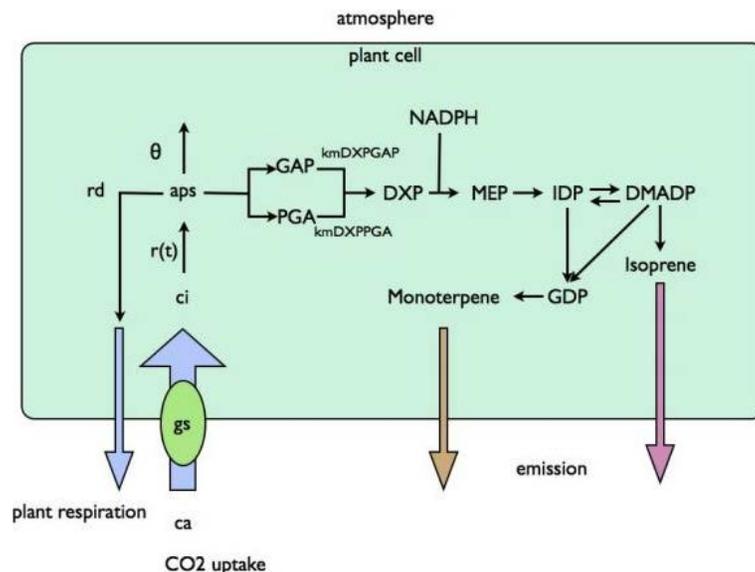


Fig. 1. Reaction pathways of the SIM-BIM emission model. Here, C_a = CO_2 concentration in the air; C_i = intercellular CO_2 concentration; g_s = stomatal conductance; A_{ps} = assimilated carbon pool; $r(t)$ = photosynthesis rate as a function of light; r_d = dark respiration rate; θ = the fraction of carbon used in plant's metabolism; $kmDXPGAP$ and $kmDXPPGA$ = Michaelis–Menten reaction coefficients; GAP = glyceraldehyde-3-phosphate; PGA = 3-phosphoglyceric aldehyde; DXP = 1-deoxy-D-xylulose 5-phosphate; MEP = 2-C-methyl-D-erythritol 4-phosphate; NADPH = nicotinamide adenine dinucleotide phosphate; IDP = isopentenyl diphosphate; DMADP = dimethylallyl diphosphate; GDP = geranyl diphosphate.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


**Comparing three
monoterpene
emission models**

S. Smolander et al.

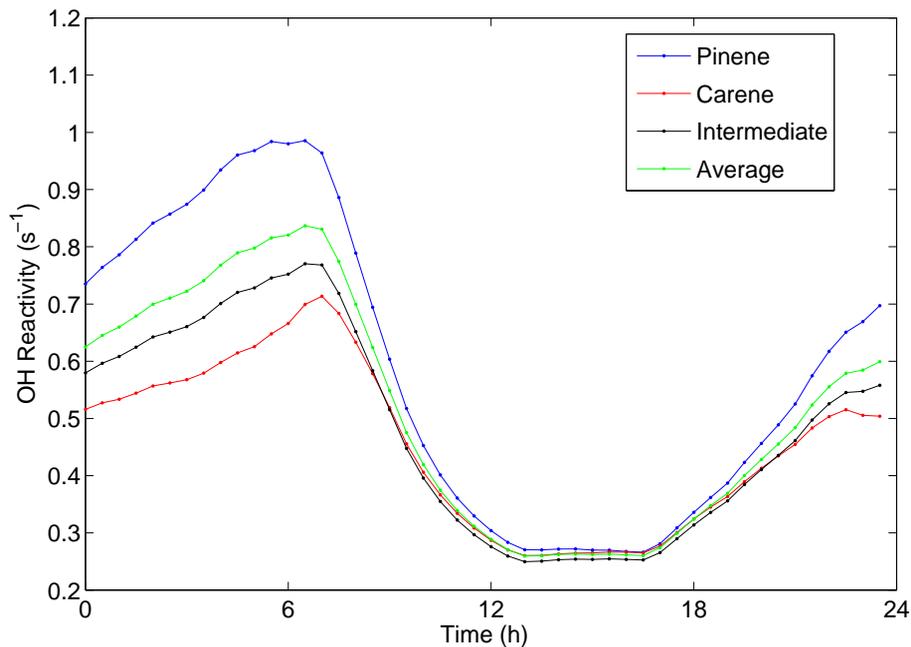


Fig. 2. Average modelled (MEGAN 2.04) diurnal profiles of OH reactivity at 14 m for the summer of year 2007 for the four chemotype scenarios (see Table 1 and Fig. 2).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

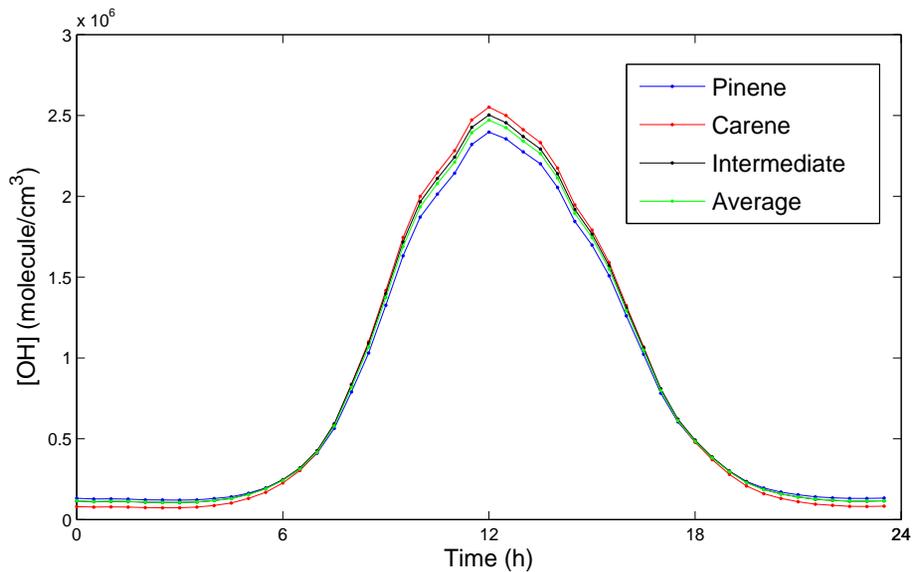


Fig. 3. Average modelled (MEGAN 2.04) diurnal profiles of OH concentration at 14 m for the summer of year 2007 for the four chemotype scenarios (see Tables 1 and 2).

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Comparing three
monoterpene
emission models

S. Smolander et al.

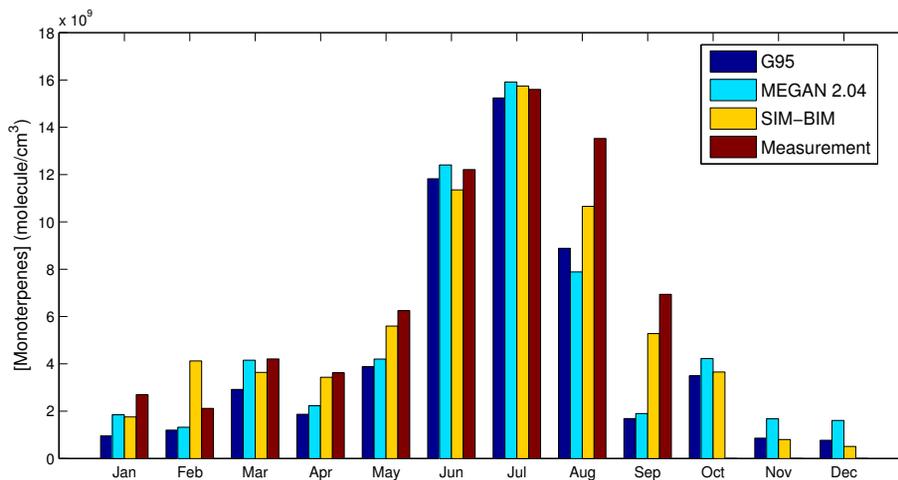


Fig. 4. Comparison of modelled (G95, MEGAN 2.04, SIM-BIM) and measured (at SMEAR II station) of average monthly monoterpene concentrations at 4 m height for year 2007.

Comparing three monoterpene emission models

S. Smolander et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

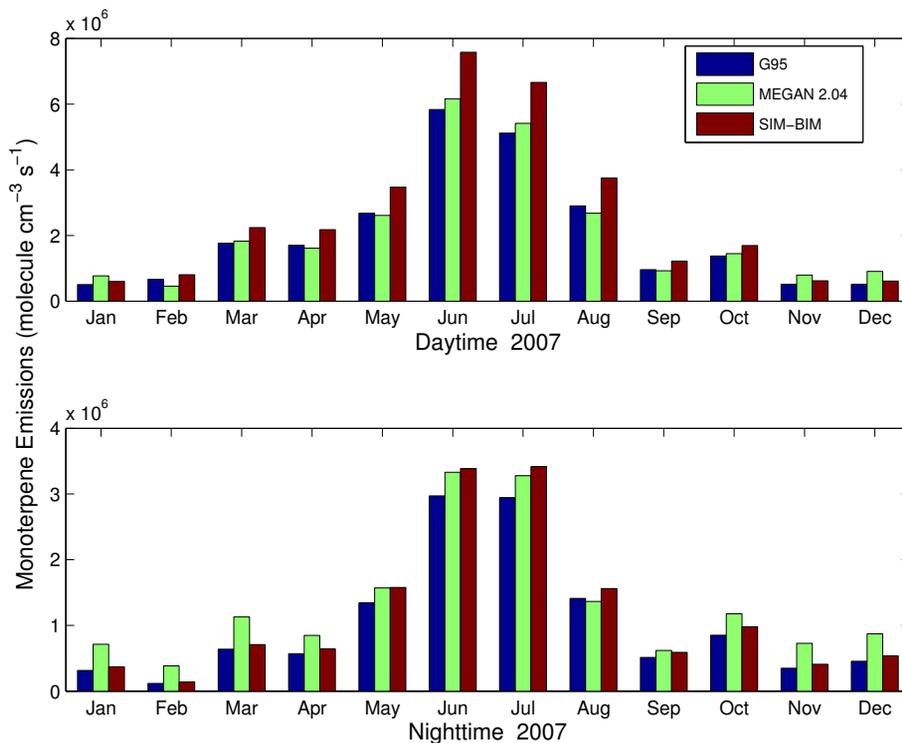


Fig. 5. Modelled (G95, MEGAN 2.04, SIM-BIM) monthly averages of daytime and nighttime monoterpene emissions at 14 m height in the canopy.

Comparing three monoterpene emission models

S. Smolander et al.

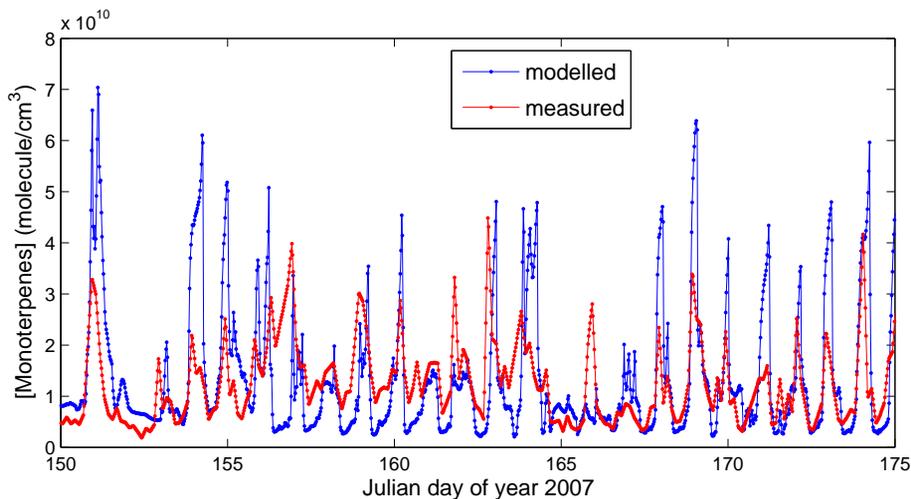


Fig. 6. Modelled (MEGAN 2.04) and measured (at SMEAR II station) monoterpene concentrations at 4 m height in June 2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Comparing three monoterpene emission models

S. Smolander et al.

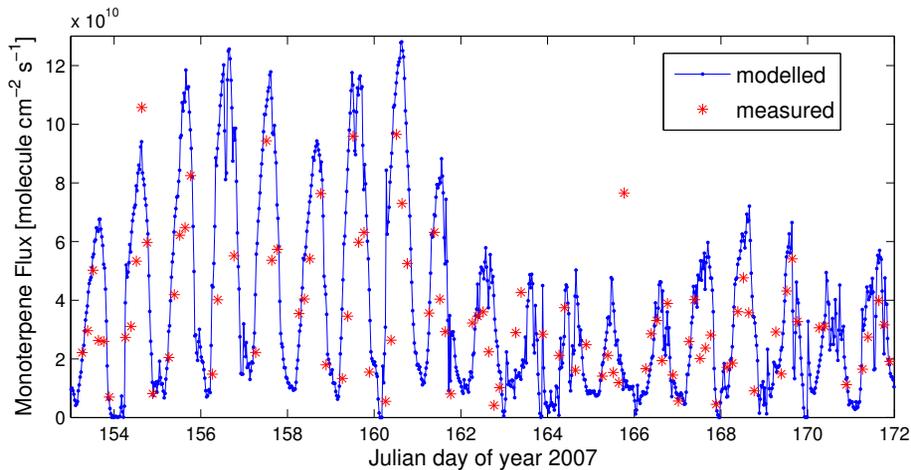


Fig. 7. Modelled (MEGAN 2.04) and measured (at SMEAR II station) monoterpene flux at 22 m height in June 2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

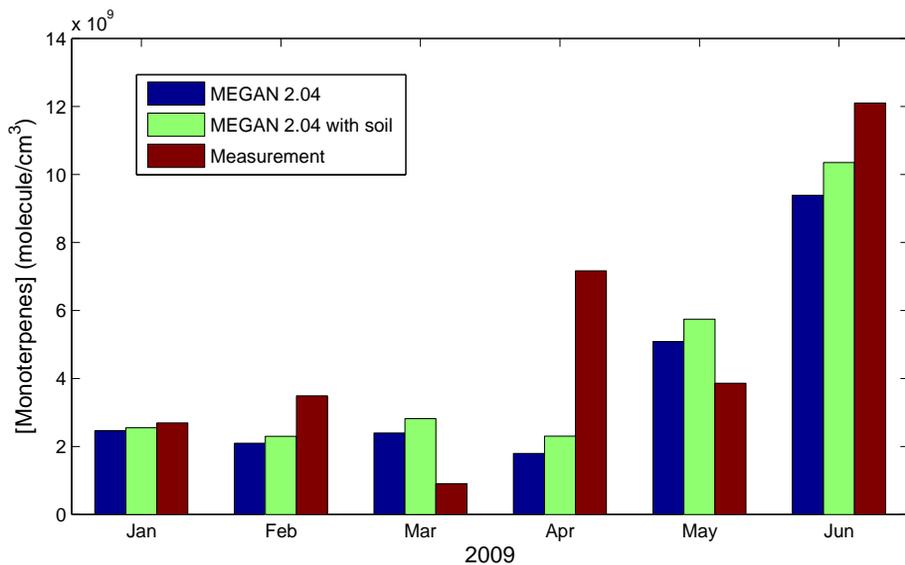


Fig. 8. Modelled (MEGAN 2.04 without and with soil emissions) and measured (at SMEAR II station) monoterpene concentrations at 4 m height in January–June in 2009.

Comparing three monoterpene emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Comparing three
monoterpene
emission models**

S. Smolander et al.

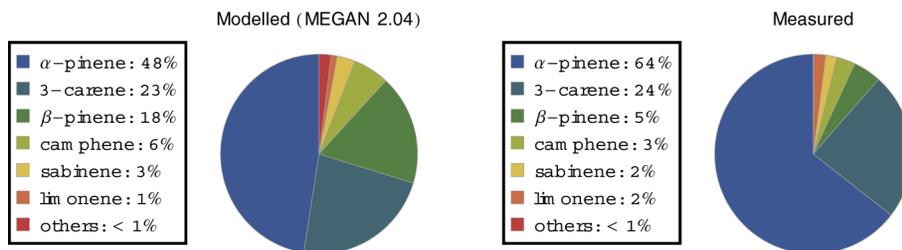


Fig. 9. Modelled (MEGAN 2.04) and measured (Hakola et al., 2009) monoterpene composition at 14 m height at SMEAR II station in summer 2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Comparing three monoterpene emission models

S. Smolander et al.

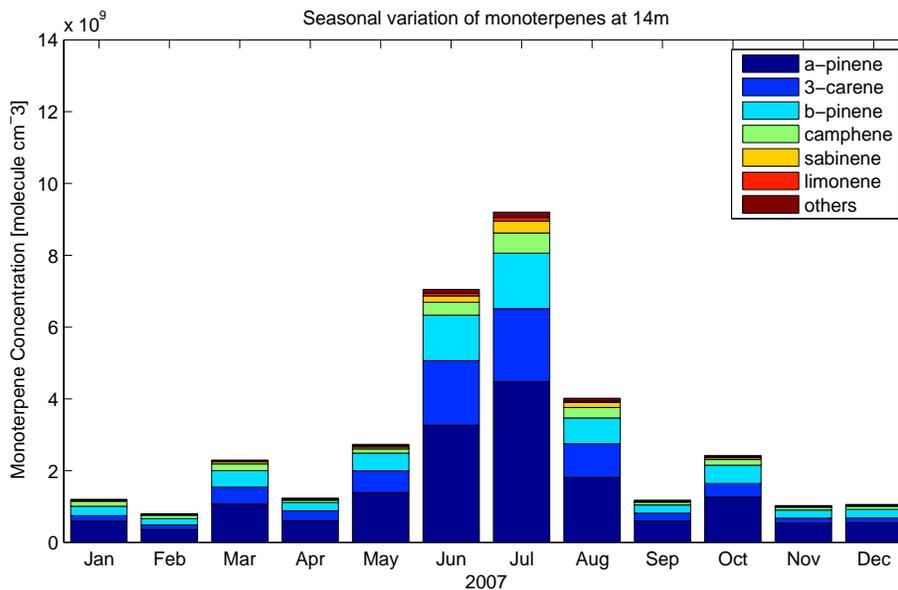


Fig. 10. Modelled (MEGAN 2.04) distribution of individual monoterpene concentrations at 14 m height for year 2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Comparing three
monoterpene
emission models

S. Smolander et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

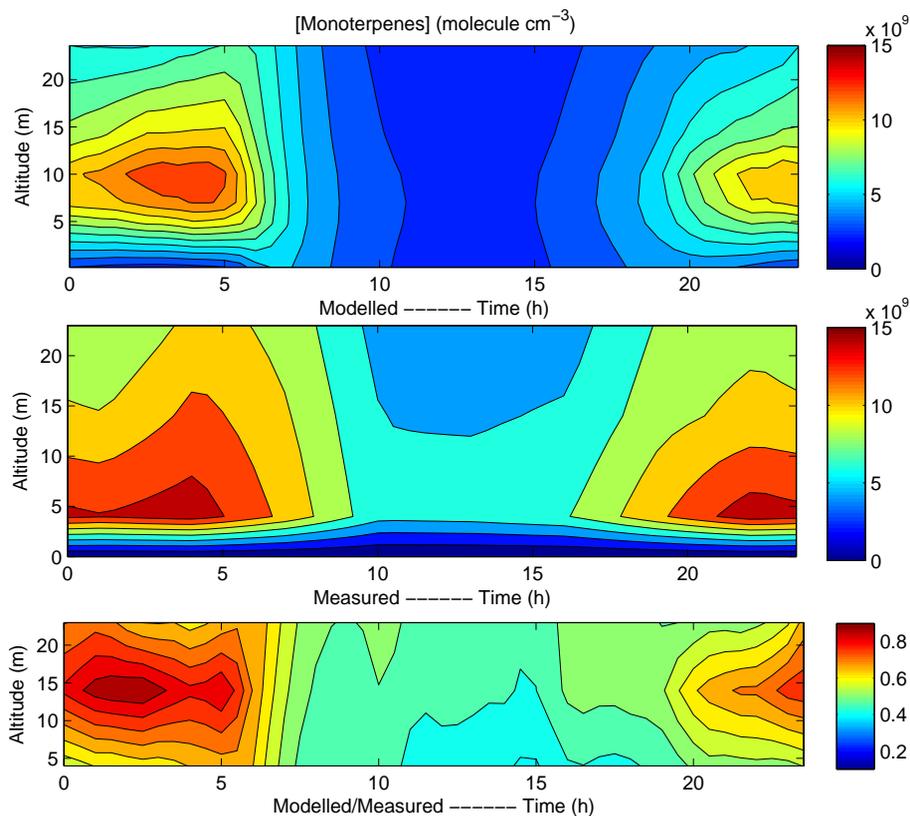


Fig. 11. Modelled (MEGAN 2.04) and measured (at SMEAR II station) monoterpene concentration vertical profiles for summer 2007.

Comparing three
monoterpene
emission models

S. Smolander et al.

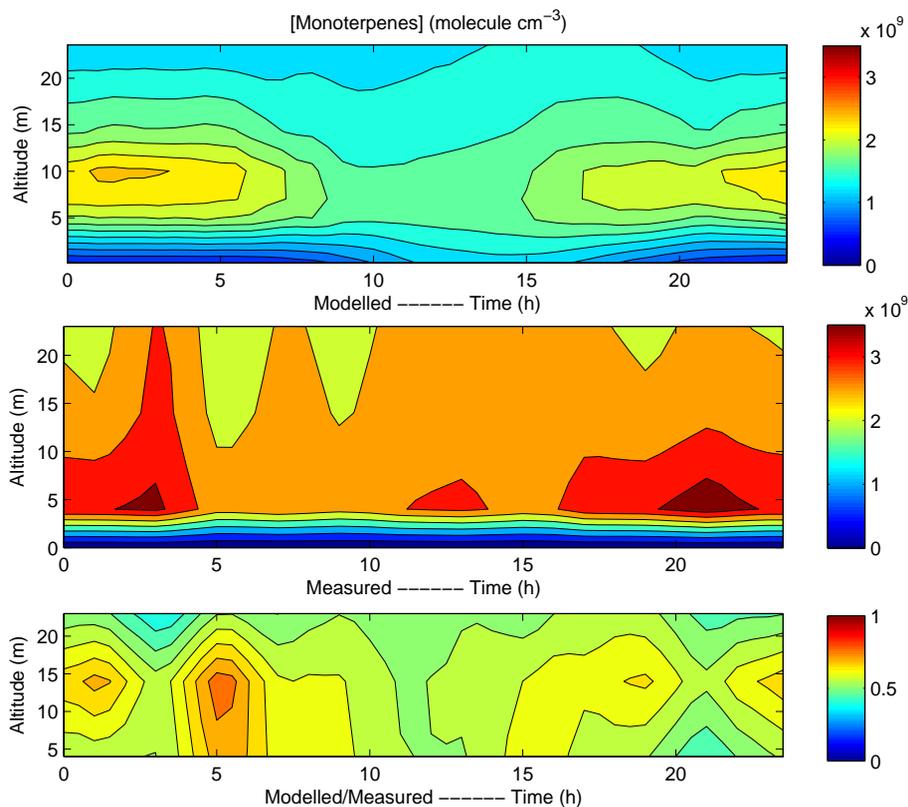


Fig. 12. Modelled (MEGAN 2.04) and measured (at SMEAR II station) monoterpene concentration vertical profiles for winter 2007.