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Hantson, Stijn; Knorr, Wolfgang; Schurgers, Guy; Pugh, Thomas; Arneth, Almut

DOI:

[10.1016/j.atmosenv.2017.02.010](https://doi.org/10.1016/j.atmosenv.2017.02.010)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Hantson, S, Knorr, W, Schurgers, G, Pugh, T & Arneth, A 2017, 'Global isoprene and monoterpene emissions under changing climate, vegetation, CO₂ and land use', *Atmospheric Environment*, vol. 155, pp. 35-45.
<https://doi.org/10.1016/j.atmosenv.2017.02.010>

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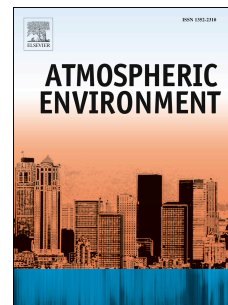
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Accepted Manuscript

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PII: S1352-2310(17)30080-8

DOI: [10.1016/j.atmosenv.2017.02.010](https://doi.org/10.1016/j.atmosenv.2017.02.010)

Reference: AEA 15183

To appear in: *Atmospheric Environment*

Received Date: 25 October 2016

Revised Date: 30 January 2017

Accepted Date: 6 February 2017

Please cite this article as: Hantson, S., Knorr, W., Schurgers, G., Pugh, T.A.M., Arneth, A., Global isoprene and monoterpene emissions under changing climate, vegetation, CO₂ and land use, *Atmospheric Environment* (2017), doi: 10.1016/j.atmosenv.2017.02.010.

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Global isoprene and monoterpene emissions under changing climate, vegetation, CO₂ and land use

Stijn Hantson¹, Wolfgang Knorr², Guy Schurgers³, Thomas A. M. Pugh^{1,4}, Almut Arneth¹

5 ¹ Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research/Atmospheric Environmental Research, Kreuzteckbahnstr. 19, 82467 Garmisch-Partenkirchen, Germany.

² Physical Geography and Ecosystem Analysis, Lund University, Sölvegatan 12, 22362 Lund, Sweden.

³ Department of Geosciences and Natural Resource Management, University of Copenhagen, Copenhagen, Denmark.

10 ⁴ School of Geography, Earth & Environmental Science and Birmingham Institute of Forest Research, University of Birmingham, Birmingham, B15 2TT, United Kingdom.

Corresponding author: Stijn Hantson (stijn.hantson@kit.edu)

15 **Abstract**

Plants emit large quantities of isoprene and monoterpenes, the main components of global biogenic volatile organic compound (BVOC) emissions. BVOCs have an important impact on the atmospheric composition of methane, and of short-lived radiative forcing agents (e.g. ozone, aerosols etc.). It is therefore necessary to know how isoprene and monoterpene emissions have changed over the past and
20 how future changes in climate, land-use and other factors will impact them. Here we present emission estimates of isoprene and monoterpenes over the period 1901-2100 based on the dynamic global vegetation model LPJ-GUESS, including the effects of all known important drivers. We find that both isoprene and monoterpene emissions at the beginning of the 20th century were higher than at present. While anthropogenic land-use change largely drives the global decreasing trend for isoprene over the
25 20th century, changes in natural vegetation composition caused a decreasing trend for monoterpene emissions. Future global isoprene and monoterpene emissions depend strongly on the climate and land-use scenarios considered. Over the 21st century, global isoprene emissions are simulated to either remain stable (RCP 4.5), or decrease further (RCP 8.5), with important differences depending on the underlying land-use scenario. Future monoterpene emissions are expected to continue their present
30 decreasing trend for all scenarios, possibly stabilizing from 2050 onwards (RCP 4.5). These results demonstrate the importance to take both natural vegetation dynamics and anthropogenic changes in land-use into account when estimating past and future BVOC emissions. They also indicate that a future global increase in BVOC emissions is improbable.

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Highlights

- Global isoprene and monoterpene emission estimates are presented (1901-2100).
- Isoprene and monoterpene emissions decrease strongly over the 20th century.
- Changes in vegetation cover drive global trends in isoprene and monoterpene emissions.
- 40 - A future global increase in BVOC emissions is improbable.

Keywords: BVOC, land use, isoprene, monoterpenes

1 Introduction

45 Isoprene and monoterpenes constitute the main part (~65%) of the biogenic volatile organic compounds (BVOCs) emitted by the terrestrial biosphere (e.g. Guenther et al., 2012). BVOCs are produced in most plant tissues, both above and below ground (Steeghs et al., 2004), and are known to be involved in plant growth, reproduction and defense. Most BVOC species, including isoprene and monoterpenes, are highly reactive with respect to major tropospheric oxidants, and they thus exert an important influence on atmospheric composition (Atkinson, 2000). Under high concentrations of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), the oxidation products of isoprene, and to a lesser extent monoterpenes, can act as precursors for photochemical ozone production in the troposphere. However, under low NO_x conditions, increased BVOC emissions lead to lower ozone production due to chain-termination reactions reducing ozone precursor concentrations (Atkinson and Arey, 2003). Generally, oxidation of organic compounds decreases hydroxyl radical concentrations, thereby increasing the lifetime of methane in the troposphere, and thus increasing radiative forcing. BVOCs, however, are now known to also regenerate hydroxyl radicals during their oxidation, which moderates this effect, although the ultimate extent of this moderation is not clear (Lelieveld et al., 2008; Fuchs et al., 2013; Hansen et al., 2017). BVOCs are also the main precursors of secondary organic aerosols (Claeys et al., 2004; Carslaw et al., 2010; Riccobono et al., 2014), and through their influence on the load and properties of atmospheric aerosol, they can influence cloud formation and characteristics, and the reflectivity of the atmosphere, with consequent impacts on the Earth's energy balance (Kanakidou et al., 2005; Rosenfeld et al., 2014; Unger, 2014). It is therefore important to understand the factors driving global BVOC emissions and how these will vary in the future.

65 The processes driving isoprene and monoterpene emissions are complex and still not fully understood (Peñuelas and Llusà, 2001; Arneth et al., 2008a; Loreto and Schnitzler, 2010 ; Harrison et al., 2013). Isoprene and monoterpenes are (side) products of leaf photosynthesis. In plants, they seem to play a role in the protection of plant membranes against high temperatures and/or oxidative stress, and act as defense compounds against pathogens and herbivores (e.g. Harrison et al., 2013; Niinemets et al., 2010a; Loreto and Schnitzler, 2010). As photosynthetic activity is a main driver of isoprene and monoterpene production, radiation and temperature, along with leaf water status, phenological state and atmospheric CO_2 mixing ratio ($[\text{CO}_2]$), affect emissions directly (on the leaf-scale) and indirectly (via plant productivity) (e.g. Guenther et al., 1995; Zimmer et al., 2000; Eisenreich et al., 2001; Niinemets et

70

75 al., 2010a; Niinemets et al., 2010b). There is also strong evidence that CO₂ directly influences the isoprene synthesis process, with inhibition under increasing [CO₂] (Possell et al., 2005; Rosenstiel et al., 2003). Whether or not similar processes operate for monoterpenes is unclear even though the similar processes of leaf metabolism for isoprene and monoterpenes would suggest this to be the case, with evidence that this is the case for at least some species (e.g. Llorens et al., 2009; Loreto et al., 2001).

80 In addition to emission effects from climate and [CO₂], which operate in principle on all emitting species in a similar way, there exists a large inter-species variability in the amount of the photosynthetic carbon uptake channeled towards the production of isoprene and/or monoterpenes (Harrison et al., 2013). The leaf-level emission capacities (emission rates under standardized conditions) depend only to a limited extent on plant family, with widely varying emission capacity even within the same genus (Kesselmeier and Staudt, 1999), but those plants that do emit BVOCs tend to emit either isoprene or monoterpenes, not both (Harrison et al., 2013). Natural changes in species distribution resulting from changing environmental conditions can therefore have important impacts on total BVOC emissions by influencing relative abundance of species with different emission capacities (Schurgers et al., 2011). In addition to natural vegetation changes, humans have transformed the Earth's terrestrial vegetation cover, with 35% of the global land surface having been converted to agriculture and pastures by the year 2000 (Klein Goldewijk et al., 2011). Crops typically have low isoprene and monoterpene emissions compared to woody vegetation, so that agricultural expansion in naturally forested areas will typically lead to a decrease in isoprene and monoterpene emissions (Rosenkranz et al., 2014; Karl et al., 2009). At least for isoprene, anthropogenic land cover change is therefore considered to be the dominant driver of change over the 20th century (e.g. Unger, 2013; Lathiere et al., 2010; Lathiere et al., 2006; Acosta Navarro et al., 2014).

100 All these previously described factors have multiple, sometimes opposing, effects on BVOC emissions and should be taken into account for both past estimates and future projections. In particular the effects of changing vegetation patterns in response to global climate change, combined with anthropogenic land-use effects have to date only been assessed in some studies for isoprene (e.g. Wu et al., 2012; Lathiere et al., 2010; Squire et al., 2014; Pacifico et al., 2012), and none for monoterpene emissions at a global scale.

105 Here we adopt an approach that accounts for natural vegetation changes as well as anthropogenic land-use change, using the LPJ-GUESS dynamic vegetation model with an integrated process-based BVOC emission scheme (Arneth et al., 2007b; Schurgers et al., 2009a) to perform estimates of global isoprene and monoterpene emissions for historical (1901-2000) and future (2001-2100) conditions. For these estimates we take into account changes in climate and the resulting natural vegetation distribution, changing [CO₂], and the impact of land transformation from natural vegetation to crop and pasture lands. We explicitly consider the positive impact of [CO₂] on photosynthesis, increasing BVOC emissions, as well as the counteracting negative direct impact of [CO₂] through CO₂ inhibition of leaf BVOC emissions. We compare the resulting range in emission estimates to previously published results, and assess the current uncertainties.

115

2 Material and methods

2.1 LPJ-GUESS vegetation model

120 We use the Lund-Potsdam-Jena General Ecosystem Simulator (LPJ-GUESS) to compute the establishment, growth and mortality of potential natural vegetation, as well as plant and soil water status on a global scale (Sitch et al., 2003; Smith et al., 2001). Carbon and water exchanges are computed on a daily time step, while establishment, growth and allocation, and mortality by episodic disturbances and competition are simulated with a yearly time step. The photosynthesis module is an adaptation of
 125 the Farquhar model (Farquhar et al., 1980) following Haxeltine and Prentice (1996). We use the global version of LPJ-GUESS with 11 plant functional types (PFTs), comprising nine tree and two grass PFTs, with vegetation parameters configured as in Ahlström et al. (2012). Adopting gap-model features, LPJ-GUESS represents important ecosystem dynamic processes such as establishment and disturbance events as stochastic processes, with a stochastic general patch-destroying disturbance with an average return
 130 interval of 100 years. For each geographical location, 25 repeated calculations (“patches”) were averaged to account for the stochastic character of vegetation growth and mortality that operates in ecosystems. Fire disturbances are represented by the SIMFIRE global fire module (Knorr et al., 2016). For each woody PFT, groups of individuals of similar age and size, or ‘cohorts’, are differentiated within these patches, and each cohort represented by a single individual. LPJ-GUESS has been widely used and evaluated at
 135 both the ecosystem and the global scale (Smith et al., 2001; Hickler et al., 2008; Morales et al., 2005; Hickler et al., 2012; Wramneby et al., 2008).

2.2 BVOC emissions module

140 The LPJ-GUESS sub-model for BVOC emissions is able to compute emission rates for both isoprene and monoterpenes. It combines the process-based leaf level emission model from Niinemets et al. (2002; 1999) with the LPJ-GUESS vegetation model as described by Arneth et al. (2007b) for isoprene, and by Schurgers et al. (2009a) for monoterpenes based on the equation:

$$BVOC_{prod} = J\alpha\varepsilon_s f_T S f_{CO_2}$$

145 The isoprene and monoterpene production in the leaf is linked to the photosynthetic electron flux J , which supplies important metabolites for BVOC synthesis in the chloroplast. α converts the electron flux into isoprene and monoterpenes with the fraction depending on the production capacity of each PFT ε_s (being the emission factors as given in Table S1 for isoprene, I_s , and monoterpenes, M_s) and on a temperature factor f_T which accounts for the higher temperature optimum of terpene production (compared to leaf electron transport). S is a seasonality factor only applied to some PFTs for isoprene
 150 production (see Table S1) and not for monoterpenes. f_{CO_2} represents the CO_2 inhibition on leaf production of isoprene and monoterpenes relative to the ~ 370 ppmv $[CO_2]$ in the year 2000. Isoprene and monoterpene production is calculated at a daily time step and all isoprene emissions produced are directly emitted, while monoterpenes can be either emitted directly or stored in a storage pool M_{stor} . Monoterpenes get released from the storage pool based on a temperature function τ , so that the total
 155 monoterpene emissions depend on both the direct monoterpene production as well as release from storage, where:

$$M_{em} = M_{prod} * (1 - f_{stor}) + M_{stor} * \tau$$

$$\frac{dM_{stor}}{dt} = M_{stor} + (M_{prod} * f_{stor}) - M_{stor} * \tau$$

160 It is assumed that coniferous trees and herbaceous vegetation store half of the monoterpenes and
 165 release these as a function of leaf temperature, whereas broadleaf trees emit all monoterpenes directly
 after production (Schurgers et al., 2009a). Adopting the concept of PFT-specific emission capacities
 (Guenther et al., 1995), the emission rates for different PFTs are scaled such that under standard
 conditions (a leaf temperature of 30°C, irradiance of 1000 μ mol PAR m⁻²s⁻¹ and ambient [CO₂] of 370
 ppmv) the emissions per unit dry leaf biomass are equal to the emission capacity (isoprene, I_s , and
 monoterpenes, M_s , as given by Arneth et al. (2007a), and Schurgers et al. (2009a); see also table S1). The
 model takes into consideration the direct and indirect responses of BVOC emissions to changing climate
 and [CO₂], including responses at the leaf as well as the ecosystem scale. A more detailed description of
 the BVOC module in LPJ-GUESS is given in Arneth et al. (2007a) and Schurgers et al. (2009a).

170 2.3 Forcing data

LPJ-GUESS was forced with monthly, 0.5 degree gridded precipitation, incoming short-wave radiation
 and temperature data for the years 1901 to 2100, taken from published simulation results by the CMIP5
 project (Taylor et al., 2012). It has to be noted that using monthly data might cause a slight lower bias in
 175 emission estimates (Ashworth et al., 2010). The climate simulations were bias corrected using CRU TS
 3.10 data following (Ahlström et al., 2012), with the addition that an additive bias correction (instead of
 the multiplicative approach in Ahlström et al., 2012) was applied for months in which the CMIP5
 precipitation was less than 5mm. Daily precipitation values were generated applying the method of Sitch
 et al. (2003) using monthly fraction of wet days. The diurnal temperature range, necessary for the BVOC
 180 simulations, was derived using a linear regression between monthly mean diurnal temperature range
 and diurnal mean temperature derived from CRU TS3.10 and applying it to the bias corrected monthly
 mean temperature. In order to match the variability unexplained by the linear regression model, a
 stochastic monthly Gaussian "noise" was added to the diurnal temperature range, with the same
 standard deviation as the residual of the linear regression. The same method was used to derive fraction
 185 of wet days from monthly mean bias-corrected precipitation (see Knorr et al., 2016). Annual atmospheric
 CO₂ mixing ratios [CO₂] are a combination of direct measurements and data obtained from ice-cores and
 future scenarios provided by CMIP5 (Meinshausen et al., 2011). CMIP5 uses emission scenarios from the
 Representative Emissions Pathways (RCP) (Van Vuuren et al., 2011), with [CO₂] reaching 538 ppmv and
 936 ppmv by 2100 for RCPs 4.5 and 8.5 respectively, compared to approximately 400 ppmv currently
 190 (Figure S1a).

Anthropogenic land-use change from natural vegetation to crops and pasture was modeled using the
 dataset of Hurtt et al. (2011), with both crop and pasture land being represented by generic C₃ and C₄
 grass plant functional types, with their relative occurrence depending on climate. For each simulation,

195 two sets of runs were performed, one with potential natural vegetation and one with only herbaceous
PFTs allowed to compete. The output from the latter runs was then assigned to the fraction of land
converted to pasture or agriculture corresponding to the RCP land-use scenario. Isoprene and
monoterpene emission capacities in croplands were set equal to those for natural C₃ and C₄ grass,
consistent with previous syntheses of emissions (e.g. Karl et al., 2009). An overview of the main BVOC
parameters for each PFT can be found in Table S1. Due to the high uncertainty associated with future
200 land-use projections, all four scenarios are considered, representing a range of possible trends in future
anthropogenic land-use (Table 1). Global maps for current and future land-use are given in Figure S2. The
anthropogenic land-use scenarios for the 21st century fall into two clear groups (Figure S1b), where land-
use under RCP 2.6 and 8.5 undergo a constant increase in crop and pasture land-use while under RCP 4.5
and 6.0 scenarios cropland expansion use shows a decrease, after reaching a peak in early 21st century.
205 To avoid confusion between future projections in land-use from future climate scenarios, we use “LU”
when we want to indicate land-use projections (e.g. land-use associated with RCP 4.5 would thus be LU
4.5). In addition to these anthropogenic land-use changes, changes in natural vegetation under changing
environmental conditions are represented by the dynamic vegetation model as described in section 2.1.

210 2.4 Simulation summary

All LPJ-GUESS simulations were run for the period 1901-2100 after a spin-up period of 500 years so that
all C-pools reached equilibrium recycling the first 30 years of the climate data. The list of simulations is
shown in Table 1. We selected climate forcing data from three well established Earth system models to
take the existing variability and uncertainty in these models into account. We use two different RCP
215 greenhouse gas scenarios for future projections – RCP 4.5 as a moderate emission scenario and RCP 8.5
as a high emission scenario – with and without a set of land-use scenarios (Table 1).

To analyze the future impact of land-use we performed runs with the same forcing data (MPI, RCP 4.5
greenhouse gas scenario) but with all four RCP future projections of land-use to identify the sensitivity of
emissions to a range of land-use assumptions, independent of climate and [CO₂].

220 In an additional set of simulations, the CO₂ inhibition effect was switched off in the model. Furthermore,
a simulations with constant atmospheric [CO₂] for the year 2000 was conducted for all setups to
separate the influence of changing climate and [CO₂] on BVOC emissions (Table 1).

3 Results

225 3.1 Present-day BVOC emission patterns and trends

Simulated present-day (1971-2000) global annual isoprene and monoterpene emissions for natural
vegetation were around 400 TgC yr⁻¹ and 30 TgC yr⁻¹, respectively (Table 2), and were not strongly
sensitive to the choice of ESM used for the climate data (Fig. S3). Global emissions of isoprene are
dominated by tropical areas, with maxima >10 gC m⁻² yr⁻¹ (Figure 2a). This stands in contrast to
230 temperate and boreal environments where emissions rarely exceed 4 gC m⁻² yr⁻¹. Maximum

monoterpene emissions differ much less between tropical, temperate and boreal regions, with typical regional values of 0.4 to 0.6 gC m⁻² yr⁻¹ (Figure 2b).

3.2 Interaction between climate, [CO₂] and natural vegetation change

235 Climate has a strong impact on BVOC emissions due to its impact on vegetation productivity and distribution, and due to the direct sensitivity of leaf BVOC emissions to temperature. When only accounting for changing climate over the study period (simulation with natural vegetation only and present day [CO₂]), both isoprene and monoterpene emissions increase strongly over the 21st century (for instance, respectively ±21% and ±23% for the RCP 4.5 scenario with MPI forcing; Figure 2).

240 Past and future natural emissions from both isoprene and monoterpenes are strongly determined by the CO₂ inhibition effect. When the CO₂ inhibition of leaf emissions is ignored, both isoprene and monoterpene emissions increase strongly under future conditions due to changes in climate (Table 2). However, when taking into account the CO₂ inhibition effect, emissions over the 21st century stay more or less stable for isoprene and decrease by 13% for monoterpenes under RCP 4.5 scenario (Table 2, 245 Figure 2). For the RCP 8.5 scenarios, with high levels of atmospheric [CO₂], a strong decrease over the 21st century is observed for both isoprene and monoterpene emissions (Figure 4a &b). As indicated in Figure 2, the future increase in atmospheric [CO₂] counteracts the increase in isoprene and monoterpene emissions due to changing climate. The strongest climate effect on emissions is obtained with RCP 8.5, as it represents the scenario with the strongest temperature increase. However, 250 atmospheric [CO₂] also increases strongly until the end of the 21st century for RCP 8.5 (Figure S1a), which more than counteracts the effects of increasing temperature and explains the marked difference between the simulated trends between RCP 4.5 on one hand and RCP 8.5 on the other (Figure 4a&b).

While interacting effects of climate and CO₂ can explain the spread in different climate scenarios, the trends for the monoterpenes are different from isoprene when only considering natural vegetation; a 255 continuous slight decline in monoterpene emissions is simulated during the 20th and first half of the 21st century (Figure 4a &b & 3). This appears at first surprising considering the similar production process of both. A large part of the difference, however, can be explained by natural changes in vegetation distribution under changing climate. Broadly speaking, the emission capacities for isoprene are higher for PFTs occurring in the tropics and decrease for PFTs growing towards the poles, the 260 opposite is true for monoterpenes (Table S1). A warming climate is simulated to lead to a widespread shift in the relative abundance of vegetation with different emission capacities in such a way that gridcell level mean isoprene emissions capacity increases over most of the globe, while the mean emission capacity of monoterpenes decreases (Figure 3). The spatial pattern of the change in emission capacity coincides relatively well with the changes in isoprene and monoterpene emissions over the 21st 265 century (Figure 1c&d). While at high northern latitudes, plants with high monoterpene emission capacities increase strongly in abundance, these barely have an impact on the global numbers because of the overall low total emissions due to the cold climate and very short growing season (Figure 1b). It is important to indicate that there often is a shift in relative abundance that affects the grid-cell mean emission factor, but is not large enough to replace the most abundant PFT (Figure 3).

270 3.3 Anthropogenic land-use

While changes in vegetation distribution in response to changing climate can have an important impact on BVOC emissions, large parts of the globe have been transformed into croplands and pastures for human use, affecting isoprene and monoterpene emission substantially (Figure 2 & 5). Over recent decades, human-induced land-use changes have led to greatly reduced isoprene emissions in the tropics, whereas a reduction in monoterpenes is simulated mainly for the mid-latitudes (Figure 5). While for natural vegetation only, isoprene emissions over the 20th century remained more or less constant, emissions are much lower when taking into account land-use changes (Figure 4c), with global isoprene emissions already for the year 1900 summing to 350 TgC yr⁻¹, compared to 400 TgC yr⁻¹ for natural vegetation. This difference is smaller for the monoterpenes, with only a reduction of 2-3 TgC yr⁻¹ for the year 1900 when anthropogenic land-use is taken into account, and no clear change in trend over the 20th century (Figure 4d). For isoprene, when taking all factors into account, the decreasing emissions over the 20th century stabilize in the RCP & LU 4.5 scenario over the 21st century with around 100 MtC yr⁻¹ lower global emissions compared to natural vegetation simulations (Figure 4c). In the RCP 8.5 case, a much stronger difference emerges between natural vegetation response and emissions when including LU 8.5 land-use changes, with the latter case showing continued decline over the 20th into the 21st century. This decline is much more pronounced than in the natural vegetation simulation (where it stems mostly from CO₂ inhibition). For monoterpene emissions, land-use changes over the 20th and 21st century do not change the overall trend when comparing the global emission sum between natural vegetation and when considering land-use (Figure 4d).

When considering the same climate forcing but different land-use scenarios, future projections for isoprene fall into two distinct groups, with higher emission under LU 6.0 and 4.5 land-use scenarios and lower emissions for LU 2.6 and 8.5 land-use scenarios (Figure 6a). A similar separation along LU scenarios is not found in future projections of monoterpene emissions, which are very similar for all land-use projections (Figure 6b). The difference in emissions between LU 4.5 and LU 8.5 land-use scenarios show contrasting spatial patterns for isoprene and monoterpenes towards the end of the 21st century (Figure 7). Due to the very high isoprene emissions over the tropical forest, any transformation from tropical forest to pasture/cropland will reduce emissions strongly (Figure 7). Tropical deforestation is higher under LU 8.5 than LU 4.5 and hence isoprene emissions decrease more strongly under the LU 8.5 than the LU 4.5 land-use scenario. Isoprene emissions are much lower outside the tropics (Figure 1a) and hence smaller changes between different land-use scenarios are observed there. The pattern for monoterpenes is more complex, with an increase in emission for the tropical forest regions under LU 8.5 while there is a decrease in emissions for the tropical savanna and temperate regions under increased land-use change (Figure 7b). These contrasting patterns over the tropics are due to the relative emission capacity of crops compared to different tropical PFTs (see Table S1). These opposite patterns globally compensate each other, explaining the very limited differences between the global total monoterpene emissions for all land-use scenarios over the 21st century (Figure 6), although with important regional patterns (Figure 7).

4 Discussion

The estimates of global annual isoprene and monoterpene emissions for the last decades of 20th century (1971-2000), including the effects of land-use change, are around 300 TgC yr⁻¹ and 26 TgC yr⁻¹ respectively. These emissions are lower than independent global estimates which give the range 350-800 and 43-177 TgC yr⁻¹ for isoprene and monoterpenes respectively, with few estimates for monoterpenes (summarized in Guenther et al., 2012, and Heald et al., 2008). The main sources of global isoprene emissions are concentrated in the tropics while monoterpene emission sources are distributed much more evenly between different biomes (Figure 1a & b). For both isoprene and monoterpenes, the distribution of global emissions simulated with LPJ-GUESS is very similar to that found in other global simulation experiments (e.g. Lathiere et al., 2006; Young et al., 2009; Heald et al., 2008; 2009; Lathiere et al., 2010; Guenther et al., 2012; Pacifico et al., 2012; Wu et al., 2012; Unger et al., 2013; Squire et al., 2014). This degree of spatial agreement between studies is partly determined by the underlying similarities between different global BVOC emission models (Arneth et al., 2008a) with all models applying light and temperature as the strongest driver of short-term emission variability, and all models assuming in some way high tropical emission capacities for isoprene and more widespread range of monoterpene emission capacity between biomes. While there is agreement on these main drivers of BVOC emissions, there are still important unknowns regarding the mechanisms of some processes, which could have important impacts on our global estimates (e.g. Loreto and Schnitzler, 2010; Harrison et al., 2013). For both isoprene and monoterpenes we assume a direct CO₂ inhibition effect on isoprene and monoterpene production. Because this process has only been described relatively recent (e.g. Rosenstiel et al., 2003; Possell et al., 2005), earlier studies on future BVOC emissions often did not take this effect into account and consequently estimated increasing BVOC emissions in the future (Lathiere et al., 2005; Sanderson et al., 2003; Wu et al., 2012), in line with our results when the CO₂ inhibition is switched off (Table 2) or when the atmospheric [CO₂] is fixed at 2000 levels (Figure 2). A CO₂ inhibition effect has been widely observed for isoprene (see e.g. Possell et al., 2005; Rosenstiel et al., 2003; summarised in Arneth et al., 2011). For monoterpenes the situation is not so clear, although some studies found evidence of it at least for some species (e.g. Llorens et al., 2009; Loreto et al., 2001). The existence (or not) of a CO₂-inhibition effect for monoterpenes remains one of the main factors of uncertainty for projecting their future emissions (e.g. Schurgers et al., 2009b; Calfapietra et al., 2013).

We find that when using only natural vegetation, simulated temporal trends of global total emissions (1900-2100) differ fundamentally between isoprene and monoterpenes. This difference reflects differences in the broad geographic distribution of isoprene vs. monoterpene sources. As a consequence, different broad areas dominate the global total. Under changing climate, shifts in vegetation composition have a large effect on emissions of both isoprene and monoterpenes (Figure 3) (e.g. Wu et al., 2012; Lathiere et al., 2010; Squire et al., 2014; Pacifico et al., 2012; Schurgers et al., 2011; Arneth et al., 2011; Arneth et al., 2008b). Importantly, these changes are widespread over the globe and often do not indicate biome shifts or shifts in dominant vegetation, but rather a change in the relative abundance of different PFTs. While some models used to calculate BVOC emissions can simulate dynamical vegetation distribution, they have problems to simulate ecosystem succession and the change in PFT composition that is the result of it. LPJ-GUESS explicitly models growth and competition among individual plants, with recurrent stochastic disturbances occurring, which results in a more realistic

representation of vegetation composition, especially for areas where multiple PFTs co-occur (Smith et al., 2001). These results therefore indicate the importance of a modeling strategy which can capture the factors determining PFT distribution and relative abundance.

355 In addition to climate-induced changes in natural vegetation, humans have changed the land-use over large parts of the globe. These anthropogenic land-use changes have important impacts on BVOC emissions due to the typically low emission capacities for isoprene and monoterpenes of crops and grasslands. A large reduction in global emissions of isoprene and monoterpenes is simulated when taking into account anthropogenic land-use (Figure 2 & 5). Furthermore a strong negative trend over the last
360 century was observed for isoprene emissions due to anthropogenic land-use change, much in line with previous results which indicated that land-use change was the dominant driver of changes in isoprene emissions over the 20th century (Unger, 2013; Lathiere et al., 2010; Lathiere et al., 2006; Acosta Navarro et al., 2014). The reduction in monoterpene emissions due to land-use change is relatively limited, probably due to the smaller difference in emission capacity between natural and anthropogenic
365 vegetation for monoterpenes relative to isoprene (Table S1), as well as the fact that land-use change is relatively limited in the boreal region, an important source region of monoterpene emissions. Ongoing land-use change over the 21st century will influence BVOC emissions further, with isoprene emissions being especially sensitive to differences in land-use scenario (e.g. Squire et al., 2014). While the observed trends are robust, much of the magnitude depends on the emission capacity used for different
370 PFTs. In our study we only use two generic cropland PFTs with associated isoprene and monoterpene emission capacities. These emission capacities are “mean” capacities and exclude emission associated to episodic events such as disturbances or due to land management. Furthermore, it is known that some crops species have much higher emissions (e.g. Karl et al., 2009; Rosenkranz et al., 2014). Although these higher-emitting crops are not currently prevalent enough to be expected to substantially influence our
375 global estimates, they may have some important regional effects on BVOC emissions, as well as providing an additional, land-use-based uncertainty to future emission projections. This is especially important when taking into account the possible future increase in bioenergy crops (oil palm, poplar, etc.), which generally have higher emission capacities than normal crops and might cause very high emissions regionally, with important implications for atmospheric pollution (Ashworth et al., 2013; Hewitt et al., 2009).

We have not quantified the effects of our simulated BVOC emissions on atmospheric chemistry. Nonetheless it is possible to make some general observations on the implications of our results based on previous literature. BVOC emissions play an important role in atmospheric chemistry at both the regional and global scales with important implications for air quality. By acting as a sink for the hydroxyl radical,
385 the primary atmospheric oxidant, they act to increase the atmospheric lifetime of methane, an important climate forcing agent (Arneth et al., 2010). A reduction in global isoprene emissions of the order of 10% has been shown to reduce the atmospheric lifetime of methane by ~5%, although multiple factors will influence the exact figure (Young et al., 2009; Unger, 2014). Thus steady, or even decreasing, global BVOC emissions can be expected to have no effect on, or even notably reduce, the climate forcing
390 resulting from methane. Products of BVOC oxidation have a catalytic effect on the production of tropospheric ozone. Although in the global mean, a reduction in BVOC emission is expected to lead to reduced tropospheric ozone concentrations, and a consequent overall cooling effect on global climate

(Unger, 2014), regionally, the direction of ozone change is strongly dependent on concentrations of nitrogen oxides. Decreased BVOC emissions in areas with low background concentrations of NO_x will act to marginally increase ozone formation (e.g. Hewitt et al., 2009), but as concentrations of ozone in such regions are generally low, the health consequences are likely to be negligible. Furthermore, as the reductions of BVOC emissions are often associated with land-use change, this is likely to be accompanied by increases in NO_x emissions; in regions rich in NO_x , which encompasses many populated areas, especially in developing countries, reduced BVOC emissions will act to reduce ozone formation, with positive consequences for health, plant growth and crop yields (Sitch et al., 2007; Mills et al., 2007; Fowler, 2008). A notable exception to this pattern of BVOC reduction is the Sahel region of Africa, where the natural vegetation changes are projected to bring about large increases in isoprene emission, which, given the concentration of polluted megacities in this region, combined with the strong insolation, is likely to contribute to high ozone episodes. The projected reductions in monoterpenes in particular can be expected to reduce the formation of secondary organic aerosols. These aerosols have been found to substantially influence cloud properties and provide a net cooling effect on climate (Paasonen et al., 2013). Decreasing the aerosol loading will also act to decrease the fraction of diffuse light at the surface, which would act to reduce vegetation productivity quite notably (Mercado et al., 2009), with potential reductions in terrestrial carbon uptake resulting. Overall, the decreased emissions of BVOC projected herein may thus contribute to a positive climate forcing, although uncertainties remain large (Unger, 2014). Further details of the likely consequences of land-use change-induced changes of BVOC emissions on air quality are reviewed in (Rosenkranz et al., 2014).

5 Summary

Our simulations indicate that global isoprene and monoterpene emissions at the beginning of the 20th century were higher than at present and are unlikely to increase over the 21st century, although with important regional variations. The main driver of the decreasing trend in isoprene emission over the past century is anthropogenic land-use change. For monoterpenes, land-use change does also play a role, but the trend is dominated by changes in natural vegetation distribution. Future isoprene and monoterpene emission will be heavily influenced by the land-use scenario followed. Isoprene emission is $> 50 \text{ MtC yr}^{-1}$ higher under the LU 4.5 and 6.0 land-use scenarios than under the LU 2.6 and 8.5 land-use scenarios. For monoterpenes, the increases and decreases will be largely regional, but may cancel out on a global scale. Over the course of the 20th century, the effects of climate and $[\text{CO}_2]$ appear to approximately compensate each other for both isoprene and monoterpenes. For the 21st century, no large changes are projected under RCP 4.5. However, a strong decrease in BVOC emissions is predicted under the RCP 8.5 climate scenario, due to the high atmospheric $[\text{CO}_2]$ and resulting CO_2 inhibition effect. These results indicate the importance of taking both natural and anthropogenic changes in land-use into account when estimating past and future isoprene emissions. They also indicate that future emission will most likely be lower than under current conditions but a large range in the magnitude of BVOC emissions is possible, depending on the climate and land-use scenarios followed (200-310 & 19-24 Mt C yr^{-1} for respectively isoprene and monoterpenes in 2100).

Due to the importance of isoprene and monoterpenes for local to regional atmospheric chemistry and air quality, our estimates can serve atmospheric modelers with a range of possible emission scenarios to estimate the aerosol and ozone formation and methane lifetime under historical and future conditions. 435 Decreases in the global load of BVOCs under scenarios with strong $[\text{CO}_2]$ increases will act to reduce methane lifetime, and thus marginally offset the radiative forcing effect of those $[\text{CO}_2]$ increases. The influence on ozone and secondary organic aerosols will be highly regional, and influenced by emissions of other trace gases, particularly nitrogen oxides, but, given the magnitude of the regional changes in BVOC emission simulated here, is likely to be notable, and may be particularly so in the Sahel region of 440 Africa. There is also evidence to suggest that the reduction of monoterpene emissions over the middle-high latitudes may contribute to a climate warming, the magnitude of which will need to be assessed with advanced chemistry-climate modelling.

Acknowledgments

445 S.H., A.A. and T.P. acknowledge support by the EU FP7 projects BACCHUS (grant agreement no. 603445) and LUC4C (grant ag. no. 603542), and W.K. and A.A. by the EU FP7 project PEGASOS (grant ag. no. 265148). We acknowledge the World Climate Research Programme's Working Group on Coupled Modelling, which is responsible for CMIP, and we thank the climate modeling groups for producing and making available their model output (Table 1). This work was supported, in part, by the German Federal 450 Ministry of Education and Research (BMBF), through the Helmholtz Association and its research programme ATMO, and the HGF Impulse and Networking fund. This is paper number 25 of the Birmingham Institute of Forest Research.

Data availability: Data are available freely upon request, please contact Stijn Hantson (stijn.hantson@kit.edu) & Almut Arneth (almut.arneth@kit.edu)

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Tables

Table 1. Summary of LPJ-GUESS simulations indicating the climate model output, the greenhouse gas climate forcing scenario and the land-use scenarios used. Land-use scenarios are named LU with the number indicating the associated RCP scenario to avoid confusion between greenhouse gas and land-use scenarios. Results with and without representation of the land-use scenario are available for each simulation setup.

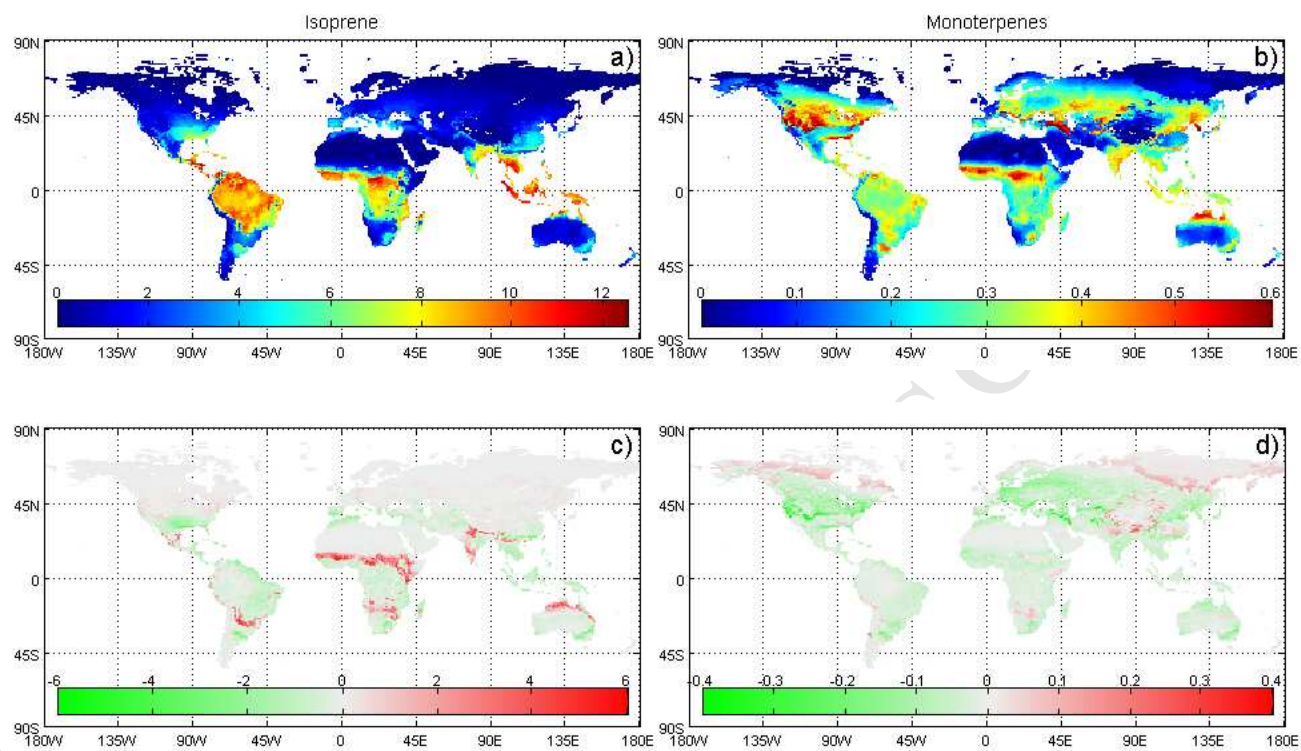
Climate Model	Full model name	Greenhouse Gas Scenario	Land-Use Scenario
MPI ¹	MPI-ESM-LR	RCP 4.5	LU 2.6
		RCP 4.5	LU 4.5
		RCP 4.5 constant CO ₂ *	LU 4.5
		RCP 4.5 without CO ₂ inhibition	LU 4.5
		RCP 4.5	LU 6.0
		RCP 4.5	LU 8.5
		RCP 8.5	LU 8.5
CCSM ²	CCSM-4	RCP 4.5	LU 4.5
		RCP 8.5	LU 8.5
IPSL ³	IPSL-CM5a-MR	RCP 4.5	LU 4.5
		RCP 8.5	LU 8.5

Modelling center or group: ¹ Max Planck Institute for Meteorology (MPI-M), ² National Center for Atmospheric Research (NCAR) ³ Institut Pierre-Simon Laplace (IPSL). * Constant CO₂ for the year 2000 applied.

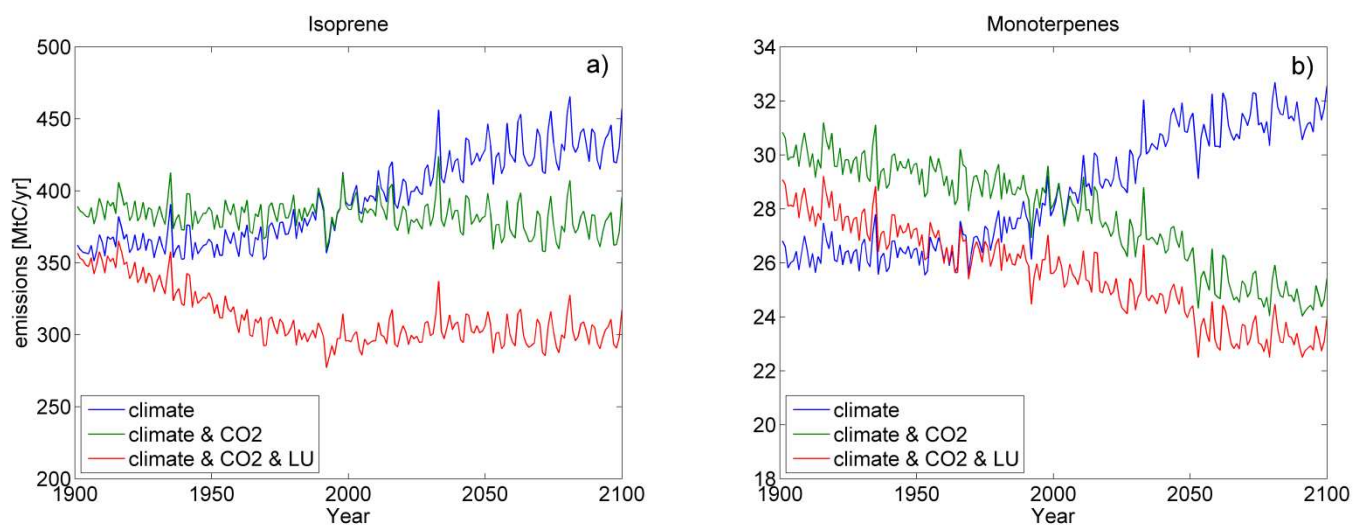
Table 2. Mean annual BVOC emissions for natural vegetation using MPI with the RCP4.5 GHG and land-use scenario.

period	CO ₂ inhibition	Isoprene (TgC/yr)	Monoterpenes (TgC/yr)
1971-2000	-	385	28.6
2071-2100	<i>On</i>	377	24.8
2071-2100	<i>Off</i>	544	35.7

Figures

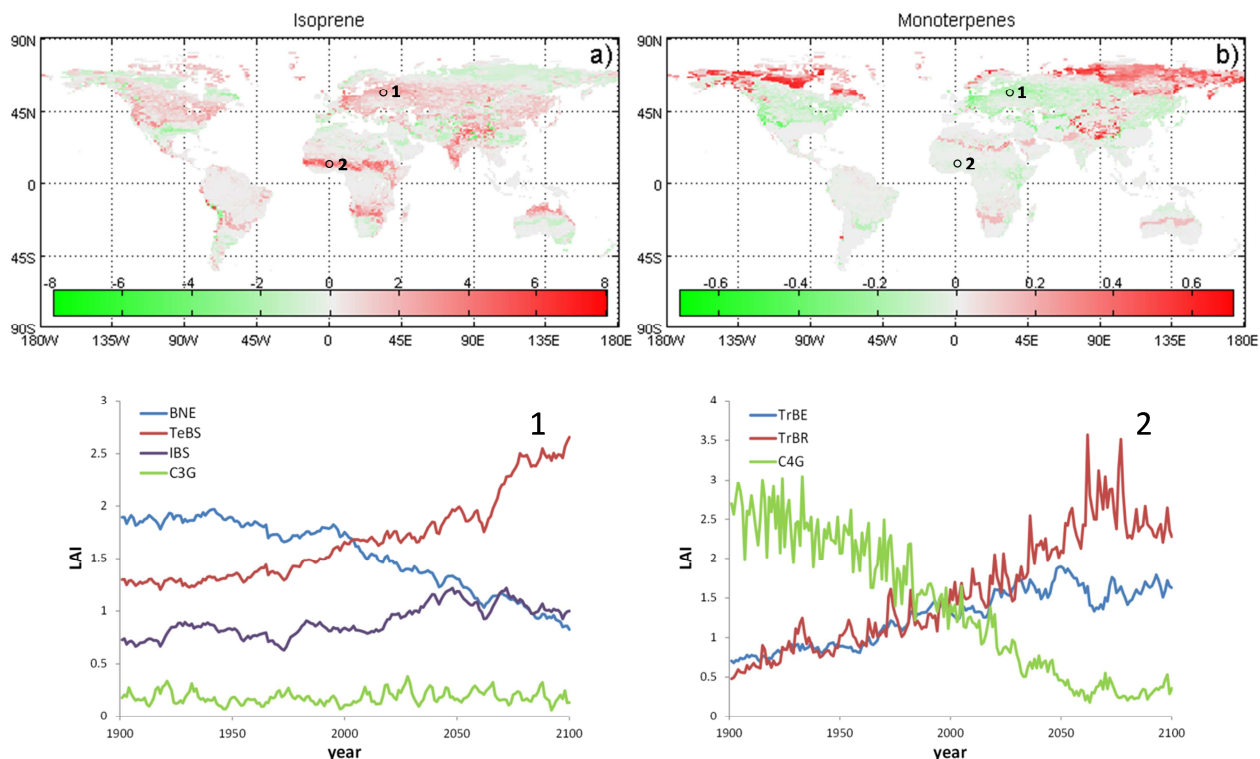


715 **Figure 1.** Present (a, b: 1971-2000) and Δ 2100-2000 (c, d) emissions in $\text{gC yr}^{-1} \text{m}^{-2}$ for Isoprene (left) and
 720 monoterpenes (right). For the Δ figures at the bottom, red indicates higher emissions in 2100 relative to
 2000 and green lower emissions. Simulations use MPI-ESM-LR climate model output with RCP 4.5
 emissions; gridcells covered with permanent ice are not represented.

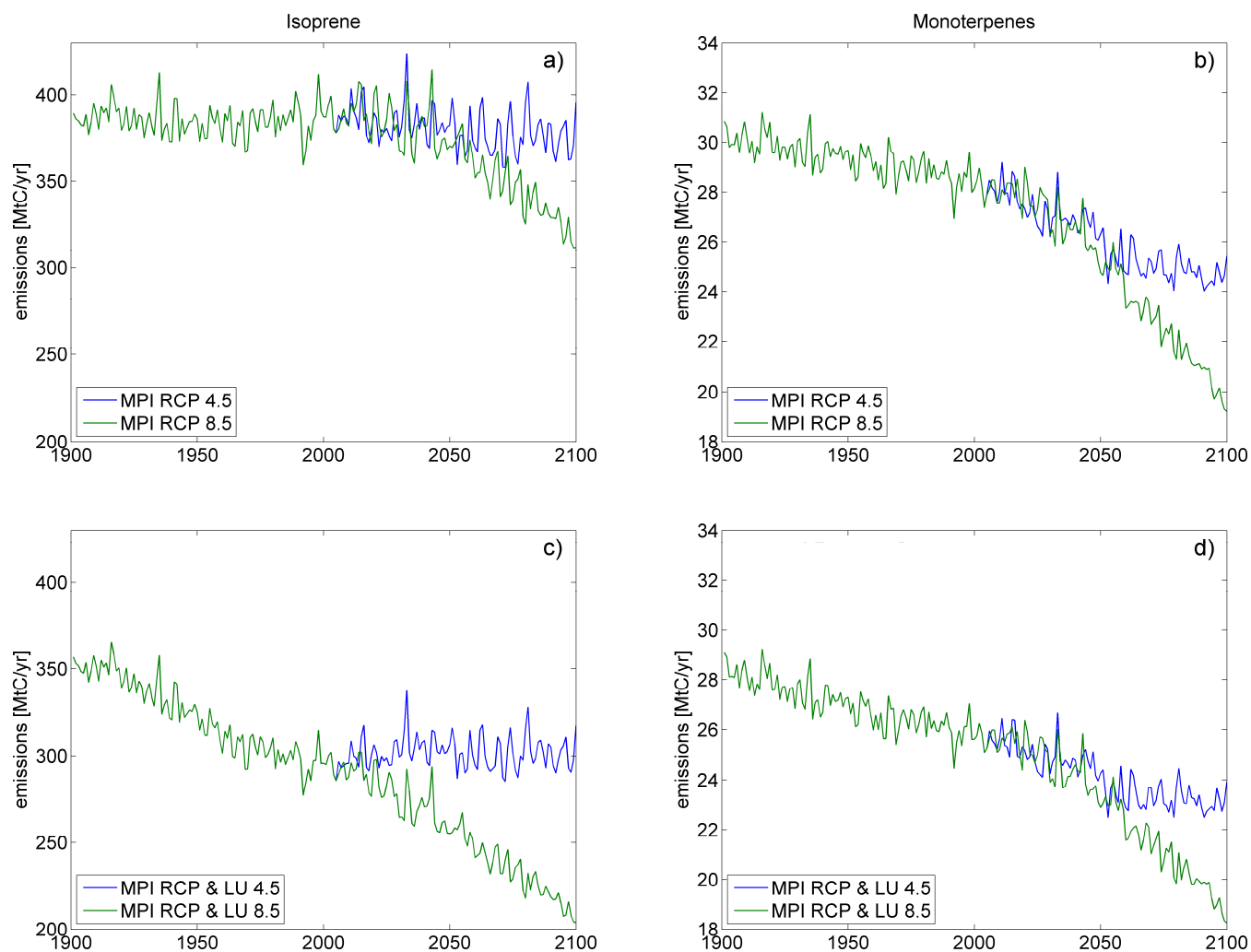


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Figure 2. Response of global annual isoprene (a) and monoterpenes (b) to changes in climate only (blue), changes in climate & atmospheric CO₂ concentrations (green) and changes in climate & atmospheric CO₂ concentrations and land-use (red). Simulations are based on RCP 4.5 climate (MPI-ESM-LR), CO₂ concentration, and land-use scenario. Atmospheric CO₂ concentrations are fixed to the values for the year 2000 in the climate only run. The factorial experiment serves to show the exemplary response to each driver and the direction of the response is similar irrespective of the RCP.

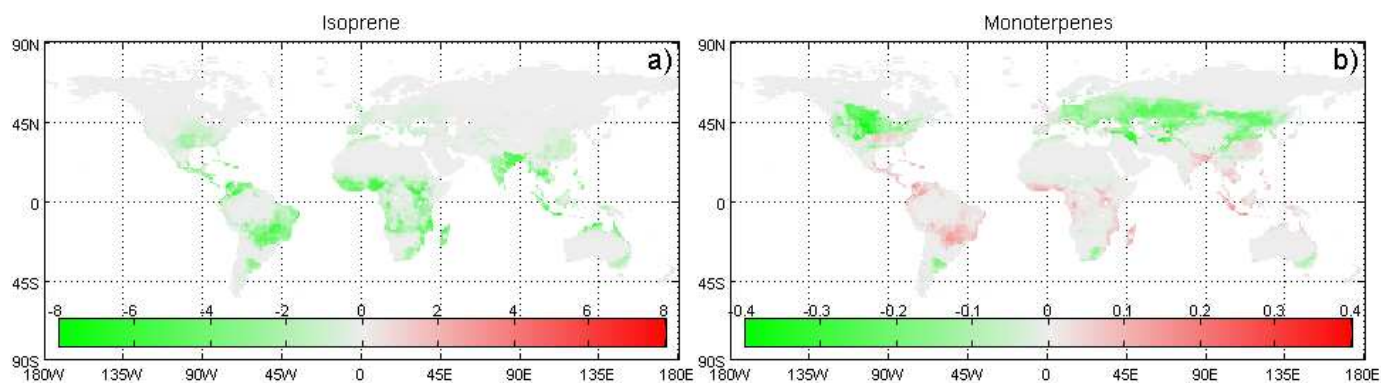


730 **Figure 3.** The difference in grid-cell mean leaf emission capacities ($\mu\text{g g}^{-1} \text{h}^{-1}$) for natural vegetation for
 future (2071-2100) minus current (1971-2000) conditions, using the MPI-ESM-LR following the RCP 4.5
 735 GHG scenario. The mean emission capacities for isoprene (a) and monoterpenes (b) are calculated
 taking into account the relative abundance of each PFT in a gridcell based on LAI. Red areas show
 regions where PFTs with higher emission capacities become more abundant, resulting in higher mean
 emission capacity at a grid-cell level. Green areas indicate regions with a decrease in mean emission
 capacity under future climate conditions; gridcells covered with permanent ice are not represented.
 Two (1 and 2) example locations show the change in LAI for each PFT. BNE: boreal needleleaved
 740 evergreen tree; TeBS: temperate broadleaved summergreen tree; C3G: C3-grass; TrBE: tropical
 broadleaved evergreen tree; TrBR: tropical broadleaved raingreen tree; C4G: C4-grass.



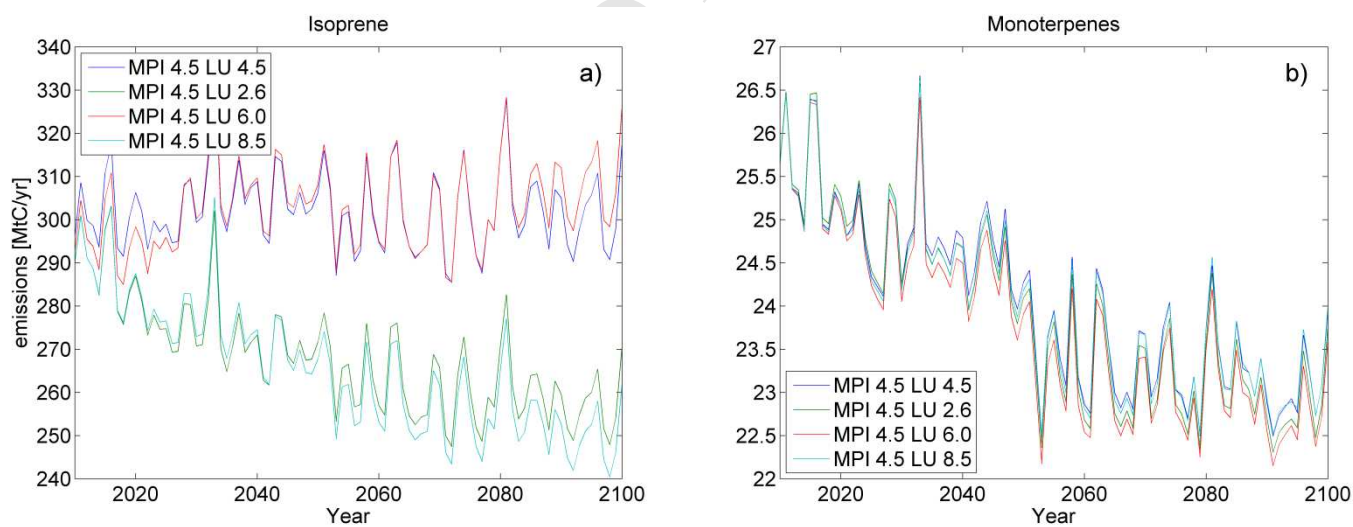
745 **Figure 4.** Isoprene (a, c) and monoterpene (b,d) emissions (Mt C yr^{-1}) for potential natural vegetation (a, b) and accounting for land-use (LU) changes (c, d). Simulations were performed using climate forcing from MPI-ESM for the emissions scenarios RCP 4.5 & 8.5, and their respective land-use change projections (see table 1). The same results are presented for climate forcing from different GCMs in figure S3.

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Figure 5. Present-day (1971-2000) BVOC emissions ($\text{g C yr}^{-1} \text{m}^{-2}$) with-without land-use change for isoprene (a) and monoterpenes (b) using MPI climate forcing under RCP 4.5 and LU 4.5; gridcells with permanent ice cover are not represented. Green areas indicate a decrease in emissions when land-use change is taken into account.



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Figure 6. Trends in future isoprene (a) and monoterpene (b) emissions (Mt C yr^{-1}), using the MPI-ESM climate model, and RCP 4.5 CO_2 pathways for all different RCP land-use (LU) scenarios.

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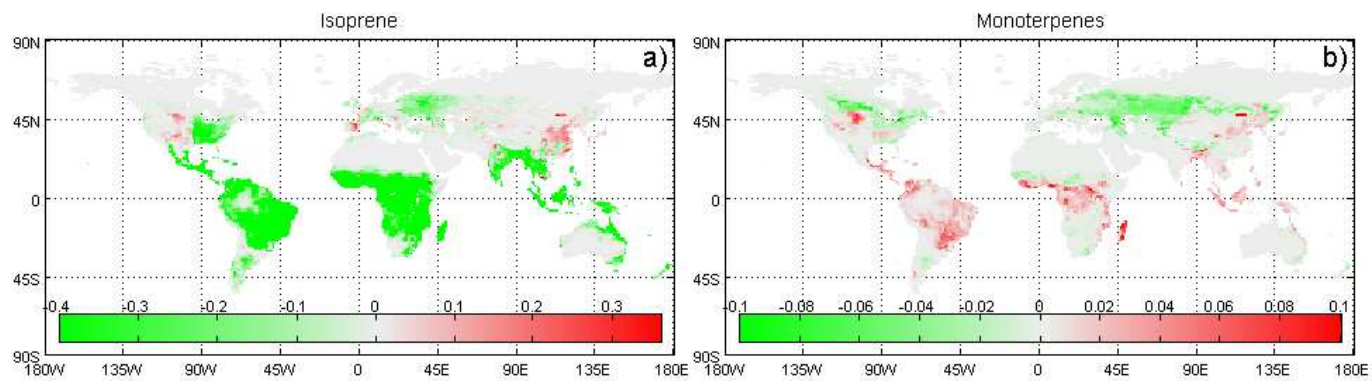


Figure 7. Difference in isoprene (a) and monoterpene (b) emissions ($\text{gC yr}^{-1} \text{m}^{-2}$) for future (2071-2100) MPI-ESM-LR RCP 4.5 climate between LU 8.5 – LU 4.5 land-use projections. Gridcells covered with permanent ice are not represented

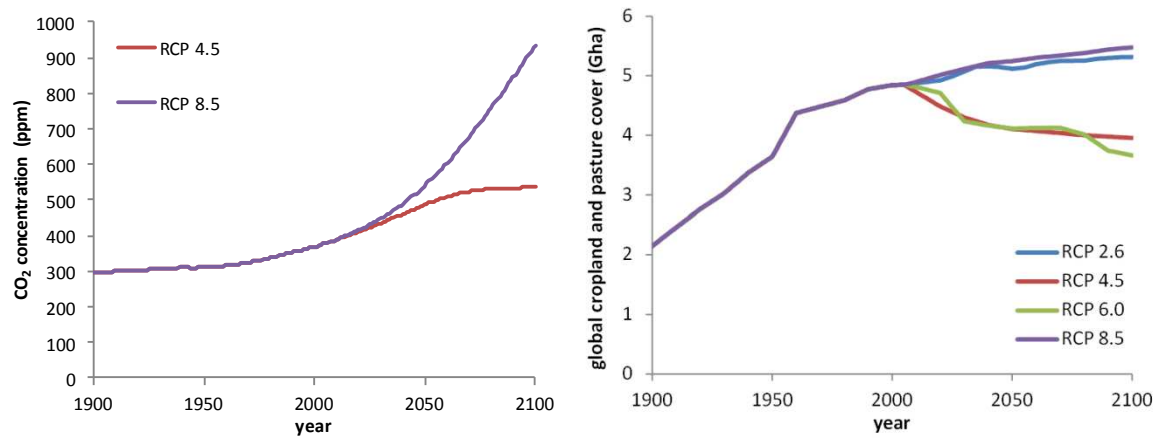
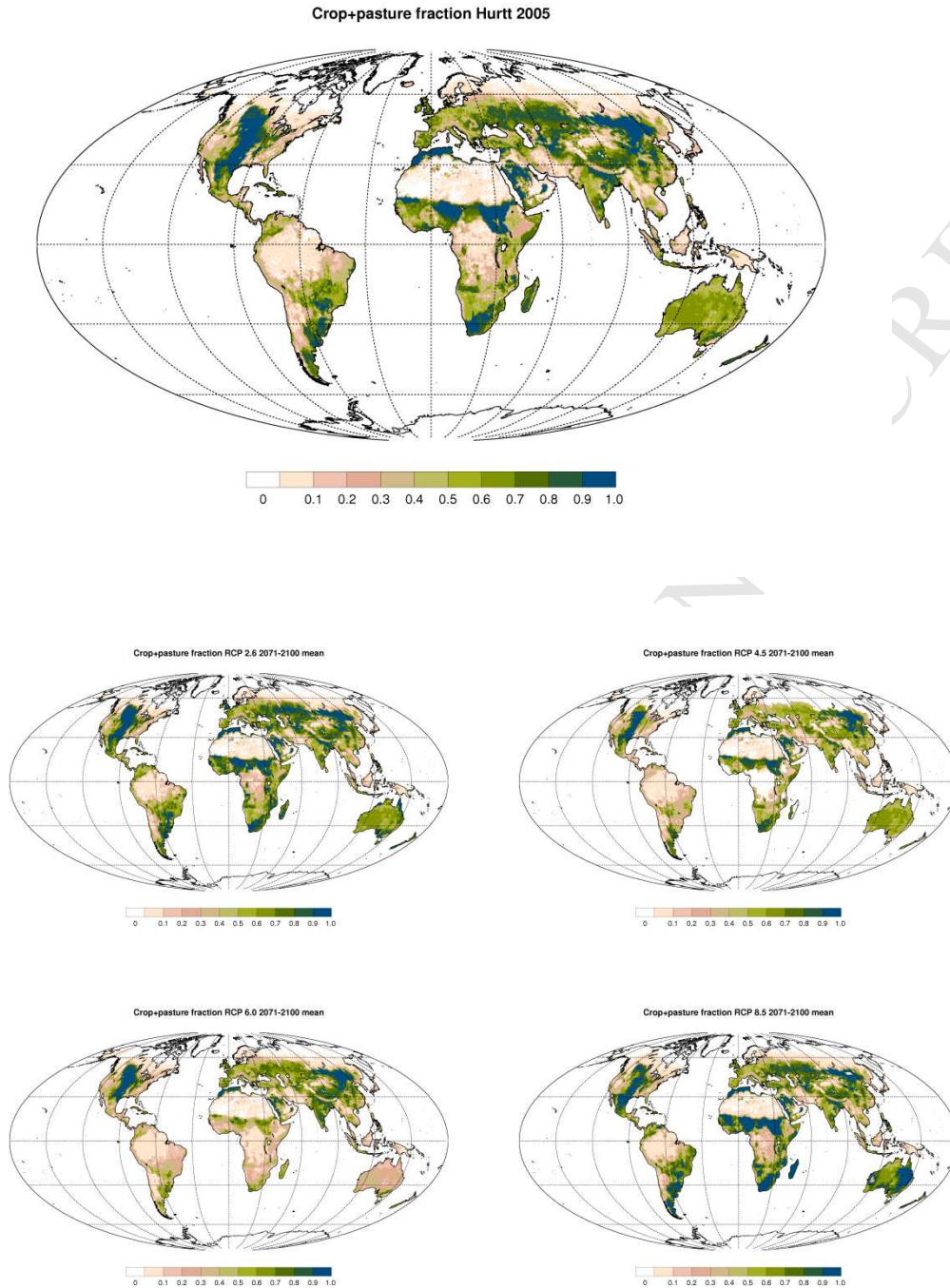


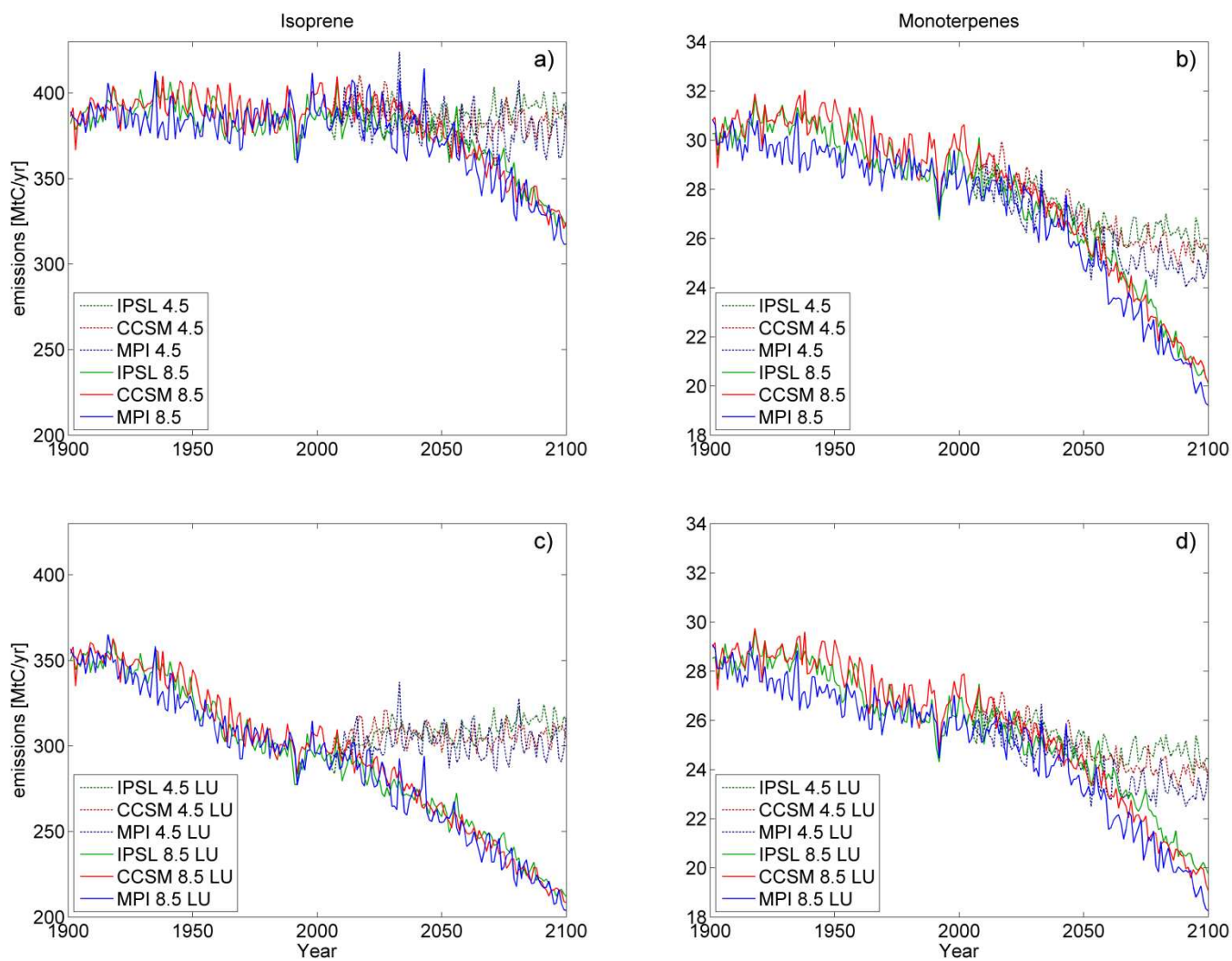
Figure S1. Atmospheric CO₂ mixing ratio and global cropland and pasture cover for historical time and projections for the future based on the different RCP scenarios used, adapted from Meinshausen et al. (2011) and Hurtt et al. (2011) respectively.

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Figure S2. Agricultural and pasture land cover for the year 2005 and the mean for the different RCP scenarios over the years 2070-2100 from Hurtt et al. (2011).



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Figure S3. Isoprene (a, c) and monoterpene (b,d) emissions (Mt C yr⁻¹) for potential natural vegetation (a, b) and accounting for land-use (LU) changes (bottom, d). Simulations were performed for a set of different GCMs, emissions scenarios, and land-use change projections (see table 1).

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Table S1. Summary of the main parameter values for the different PFTs considered largely based on the values presented in Arneth et al. (2007a) and Schurgers et al. (2009a). I_s : PFT specific isoprene emission capacity, M_s : PFT specific isoprene emission capacity, f_{stor} : monoterpene storage fraction, BNE: boreal needleleaved tree, BINE: shade intolerant boreal needleleaved tree, BNS: boreal needleleaved summergreen tree, TeBS: temperate broadleaved summergreen tree, TeIBS: shade intolerant temperate broadleaved summergreen tree, TeBE: temperate broadleaved evergreen tree, TrBE: tropical broadleaved evergreen tree, TrIBE: shade intolerant tropical broadleaved evergreen tree, TrBR: tropical broadleaved evergreen tree, C3G: C3 grass, C4G: C4 grass. The term “tree” is used in a general sense and includes all woody vegetation.

PFT	I_s ($\mu\text{g g}^{-1} \text{h}^{-1}$)	Isoprene seasonality	M_s ($\mu\text{g g}^{-1} \text{h}^{-1}$)	f_{stor} (-)
BNE	8	0	4.8	0.5
BINE	8	0	4.8	0.5
BNS	8	1	4.8	0.5
TeBS	45	1	1.6	0
TeIBS	45	1	1.6	0
TeBE	24	0	1.6	0
TrBE	24	0	0.8	0
TrIBE	24	0	0.8	0
TrBR	45	0	2.4	0
C3G	16	1	1.6	0.5
C4G	8	0	2.4	0.5

Highlights

- Global isoprene and monoterpene emission estimates are presented (1901-2100).
- Isoprene and monoterpene emissions decrease strongly over the 20th century.
- Changes in vegetation cover drive global trends in isoprene and monoterpene emissions.
- A future global increase in BVOC emissions is improbable.