Unaccounted impacts of diterpene emissions on atmospheric aerosol loadings

Ana Maria Yáñez-Serrano[1,2,3], Josep Peñuelas[2,3], Oriol Jorba[4], Frans Graeffe[5], Melissa Meder[5], Olga Garmash[6], Yanjun Zhang[7], Haiyan Li[5], Yuanyuan Luo[5], Arnaud Praplan[7], Heidi Hellén[7], Siegfried Schobesberger[8], Lejish Vettikkat[8], Steven Thomas[5,7], Theo Kurten[9], Ditte Taipale[5], Efstratios Bourtsoukidis[10], Alex Guenther[11], and Mikael Ehn[5].

[1]{IDAEA-CSIC, 08034, Barcelona, Spain}
[2]{CREAF, E08193 Bellaterra (Cerdanyola del Vallès), Catalonia, Spain}
[3]{CSIC, Global Ecology Unit, CREAF-CSIC-UAB, E08193 Bellaterra (Cerdanyola del Vallès), Catalonia, Spain}
[4]{Barcelona Supercomputing Center - Centro Nacional de Supercomputación, Barcelona, Spain}
[5] {Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki, 00014, Finland}
[6] {Department of Chemistry, University of Copenhagen, DK-2100, Copenhagen, Denmark}
[7] {Atmospheric Composition Research, Finnish Meteorological Institute, Helsinki, 00101, Finland}
[8] {Department of Technical Physics, University of Eastern Finland, 70211 Kuopio, Finland}
[9]{University of Helsinki, Department of Chemistry and Institute for Atmospheric and Earth System Research (INAR), P.O. Box 55, 00014 Helsinki, Finland}
[10]{Climate and Atmosphere Research Center (CARE-C), The Cyprus Institute, Nicosia, Cyprus}
[11]{Department of Earth System Science, University of California, Irvine, CA, USA}

Supplementary information

1. Diterpene species list

List of different diterpene species that have been reported as emissions:

(ent)kaurene, phyllocladene, abietatriene, cembrene, manoyl oxide, verticillol, rimuene, sandaracopimaradiene, 13-epi-manool oxide, norabieta-8,11,13-triene, 16-hydroxykaurene or 3-methylene-5-αandrostane[1–5].

2. Literature review on diterpene observations

All available kaurene emission reported in literature are listed in table SI. Table 2.1. For modelling BVOC emission rates, emission factors (emissions at 30ºC) are needed. For temperature dependent BVOCs, like expected for kaurene, an emission factor can be derived using the relationship between temperature and a temperature dependent emission rate:

$$E = E_{30} exp\left(\beta (T - T_{30})\right)$$

Where *E* is the emission rate at a given temperature, E_{30} is the emission rate at the standard condition of 30ºC, β is an empirical coefficient, and *T* is temperature[6]. For deriving the emission factor of kaurene for those studies not reporting emissions at 30ºC, we used a β of 0.15 °C^{-1}. This value is the average β obtained from those studies in the literature review that reported it, and was used to derive the basal emission factors for the studies that not reported standard conditions, to be used in MEGAN modelling[7–10].

Study	Year	Location	Plant species	Considered PFT	Diterpene species	Instrumentation	Ambient mixing ratio ppb	Emission in nmol m-2 s-1	Emission in µg gdryweight-1 h-1	Standard Leaf Area (SLA) m-2 g-1	Emission in µg m-2 h-1	Temperature of measurements ºC	β-factor	Emission in µg m-2 h-1*LAI=5 One side leaf approach	Standardized emissions E30 LA normalized EF, ug m-2 h-1	Used for modelling in this study?	Comments
Matsunaga et al., 2012	2009-10	Tokyo, Japan	*C. Japonica*	Needle leaf tree	Kaurene	GC-MS/GC-FID	-	-	1.1E+00	7.0E-03	1.5E+02	30	0.15	750.0000	750.0000	YES	very high emissions
Matsunaga et al., 2012	2009-10	Miyazaki, Japan	*C. Japonica*	Needle leaf tree	Kaurene	GC-MS/GC-FID	-	-	8.7E+00	7.0E-03	1.2E+03	30	0.22	6242.8571	6242.8571	YES	very high emissions
Matsunaga et al., 2012	2009-10	Tokyo, Japan	*C. Obtusa*	Needle leaf tree	Kaurene	GC-MS/GC-FID	-	-	2.2E+00	5.9E-03	3.7E+02	30	0.21	1864.4068	1864.4068	YES	very high emissions
Matsunaga et al., 2012	2009-10	Miyazaki, Japan	*C. Obtusa*	Needle leaf tree	Kaurene	GC-MS/GC-FID	-	-	9.9E-01	5.9E-03	1.7E+02	30	0.20	838.9831	838.9831	YES	very high emissions
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shrub/bush	Kaurene	GC-MS	-	-	3.1E-06	5.3E-03	5.9E-04	30	0.09	0.0029	0.0029	YES	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shrub/bush	Kaurene	GC-MS	-	-	3.3E-06	4.8E-03	6.9E-04	30	0.07	0.0035	0.0035	YES	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shrub/bush	Kaurene	GC-MS	-	-	2.8E-06	4.3E-03	6.7E-04	30	0.12	0.0033	0.0033	YES	
Yáñez-Serrano et al., 2018	2017	Laboratory	*Halimium halimifolium*	Shrub/bush	Kaurene	GC-MS /PTR-TOF-MS	-	3.4E-02	2.1E-01	6.3E-03	3.3E+01	25	0.15	166.4640	352.4043	YES	
Fisher et al., 2021	2016	Hyytiälä, Finland	*Hyttiala*	Needle leaf tree	sum	PTR-TOF-MS	-	1.5E-04	9.1E-04	6.2E-03	1.5E-01	19	0.15	0.7344	3.8240	YES	

Thomas et al., 2022	2019	Hyytiälä, Finland	*Betula pubescens*	Broadleaf Deciduous Tree	Sum	Vocus-PTR	-	-	6.0E-04	1.2E-02	4.8E-02	30	0.04	0.2402	0.2402	YES	only one replicate for this PFT
Vettikkat et al., 2023	2021	Siikaneva, Finland	*Fen*	Grass/crops	sum	Vocus-PTR	-	-	-	-	1.1E+01	30	0.18	54.0000	54.0000	YES	only one replicate for this PFT
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	Sum	GC-MS	-	-	9.0E-03	5.0E-03	1.8E+00	30	0.06	9.0909	9.0909	YES	Branch; Fig. 9
Hiura et al., 2023	?	Across Japan	*C. Japonica*	Needle leaf tree	Kaurene	GC-MS/GC-FID	-	-	5.5E+00	7.0E-03	7.9E+02	-	-	3951.4286	3951.4286	NO	Unknown temperature, and very high emissions
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Cembrene	GC-MS	-	-	2.3E-05	5.3E-03	4.3E-03	30	0.12	0.0214	0.0214	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Cembrene	GC-MS	-	-	1.2E-05	4.8E-03	2.5E-03	30	0.10	0.0126	0.0126	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Cembrene	GC-MS	-	-	1.1E-05	4.3E-03	2.7E-03	30	0.13	0.0133	0.0133	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Manoyl oxide	GC-MS	-	-	1.3E-05	5.3E-03	2.5E-03	30	0.12	0.0124	0.0124	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Manoyl oxide	GC-MS	-	-	1.8E-05	4.8E-03	3.8E-03	30	0.11	0.0191	0.0191	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Manoyl oxide	GC-MS	-	-	2.1E-05	4.3E-03	5.0E-03	30	0.14	0.0252	0.0252	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	sum	GC-MS	-	-	5.0E-05	5.3E-03	9.3E-03	30	0.12	0.0467	0.0467	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	sum	GC-MS	-	-	6.1E-05	4.8E-03	1.3E-02	30	0.08	0.0632	0.0632	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	sum	GC-MS	-	-	6.0E-05	4.3E-03	1.4E-02	30	0.14	0.0703	0.0703	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Verticillol	GC-MS	-	-	3.2E-06	5.3E-03	6.1E-04	30	0.08	0.0030	0.0030	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Verticillol	GC-MS	-	-	2.2E-06	4.8E-03	4.6E-04	30	0.06	0.0023	0.0023	NO	
Haberstroh et al., 2018	2017	Vila Viçosa, Portugal	*Cistus ladanifer*	Shurb/bush	Verticillol	GC-MS	-	-	1.6E-06	4.3E-03	3.9E-04	30	0.13	0.0019	0.0019	NO	
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	cambrene A	GC-MS	-	-	2.1E-02	5.0E-03	4.1E+00	30	0.07	20.7071	20.7071	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	cembrene	GC-MS	-	-	2.1E-02	5.0E-03	4.2E+00	30	0.11	20.8081	20.8081	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	rimuene	GC-MS	-	-	2.9E-03	5.0E-03	5.9E-01	30	0.12	2.9293	2.9293	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	Sum	GC-MS	-	-	1.5E-03	5.0E-03	3.0E-01	30	0.15	1.5152	1.5152	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	1.5E-03	5.0E-03	3.0E-01	30	0.12	1.5152	1.5152	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	9.0E-04	5.0E-03	1.8E-01	30	0.08	0.9091	0.9091	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	3.0E-04	5.0E-03	6.1E-02	30	0.13	0.3030	0.3030	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	7.0E-04	5.0E-03	1.4E-01	30	0.11	0.7071	0.7071	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	5.0E-04	5.0E-03	1.0E-01	30	0.15	0.5051	0.5051	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Picea Abies*	Needle leaf tree	unidentified	GC-MS	-	-	8.0E-04	5.0E-03	1.6E-01	30	0.10	0.8081	0.8081	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Pinus sylvestris*	Needle leaf tree	abietadiene	GC-MS	-	-	2.0E-04	6.2E-03	3.2E-02	30	0.18	0.1613	0.1613	NO	the needles were heated in the over

Helin et al., 2020	2020	Hyytiälä, Finland	*Pinus sylvestris*	Needle leaf tree	san-daracopimara-diene	GC-MS	-	-	5.0E-04	6.2E-03	8.1E-02	30	0.10	0.4032	0.4032	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Pinus sylvestris*	Needle leaf tree	Sum	GC-MS	-	-	1.0E-03	6.2E-03	1.6E-01	30	0.11	0.8065	0.8065	NO	the needles were heated in the over
Helin et al., 2020	2020	Hyytiälä, Finland	*Pinus sylvestris*	Needle leaf tree	unidentified	GC-MS	-	-	7.0E-04	6.2E-03	1.1E-01	30	0.10	0.5645	0.5645	NO	the needles were heated in the over
Edtbauer et al., 2021	2016–2018	Central Amazonia, Brazil	ATTO	N/A	sum	PTR-TOF-MS	-	-	3.0E-01	-	-	-	-	-	-	NO	average day bryophyte emission
Li et al., 2020	2019	Kevo, Finland	Thawing permafrost	N/A	Sum	PTR-TOF-MS	-	1.1E-02	-	-	-	-	-	-	-	NO	Soil emissions
Yee et al., 2018	2014	Central Amazonia, Brazil	Rural site - wet season	N/A	sum	SVTAG	8.6E-05	-	-	-	-	-	-	-	-	NO	Ambient air
Yee et al., 2018	2014	Central Amazonia, Brazil	Rural site/dry season	N/A	sum	SVTAG	6.0E-05	-	-	-	-	-	-	-	-	NO	Ambient air
Li et al. 2020	2018	Bilos, France	Landes forest	N/A	Sum	PTR-TOF-MS	3.0E-03	-	-	-	-	-	-	-	-	NO	Ambient air

Table S.I. 2.1: All reported studies with kaurene vegetation emission or ambient mixing ratio. For instrumentation, GC-MS stands for Gas Chromatography Mass Spectrometry, GC-FID stands for Gas Chromatography Flame Ionization Detector, PTR-TOF-MS stands for Proton Transfer Reaction Time of Flight Mass Spectrometer and Vocus-PTR stands for Vocus Proton Transfer Reaction Mass Spectrometer. The procedure to obtain standardized emission factors normalized to leaf area are shown in the different columns.

Table S.I. 2.2.: Table summarizing emission factors according to plant species which are classified in plant functional types (PFT), together with their average PFT emission factor standardized at 30ºC and to a Leaf Area Index (LAI) of 5 m^2 m^{-2} for using the one leaf approach.

Plant Species	**Considered PFT**	**Standardized emissions E30 LAI normalized EF, µg m^{-2} h^{-1}**		**Standardize emissions E30 LA normalized EF, µg m^{-2} h^{-1}**
Fen	grass	54	average grass	54.00
Betula pubescens	Broadleaf deciduous tree	0.24	average broadleaf tree	0.24
Picea abies	Needle leaf tree	9.091		
P. sylvestris	Needle leaf tree	0.806		
C. Obtusa	Needle leaf tree	1351		
C. Japonica	Needle leaf tree	3496	average needle leaf tree	1214.51
C. ladanifer	Shrub/bush	0.003		
H.halimnifolium	Shrub/bush	352.404	average Shrub/bush	176.20

3. Modelling of kaurene emissions and SOA production from kaurene oxidation

3.1. Seasonal average emission rates and SOA surface concentration for kaurene

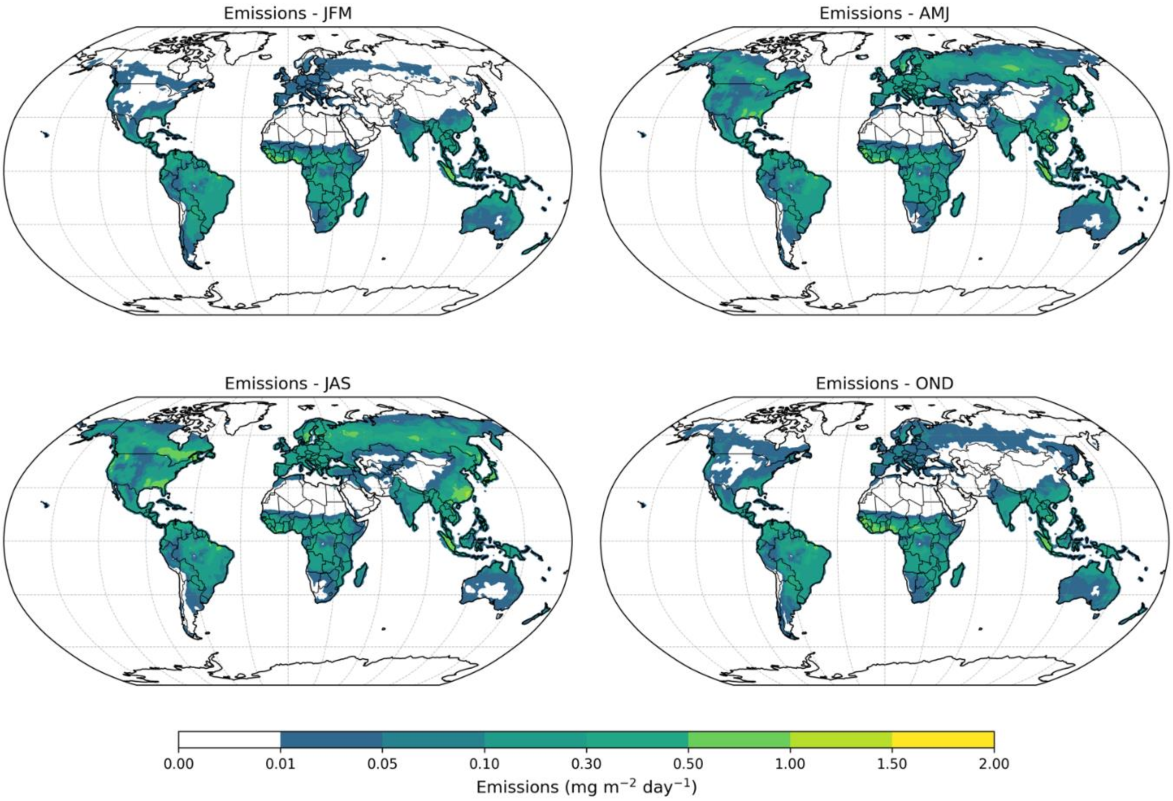

Figure SI 3.1.1: Seasonal average kaurene emission rates for 2018 where **only 10%** of the vegetation emits kaurene. (JFM: January-February-March; AMJ: April-May-June; JAS: July-August-September; OND: October-November-December.) **Scale 0-2 mg m^{-2} day^{-1}**

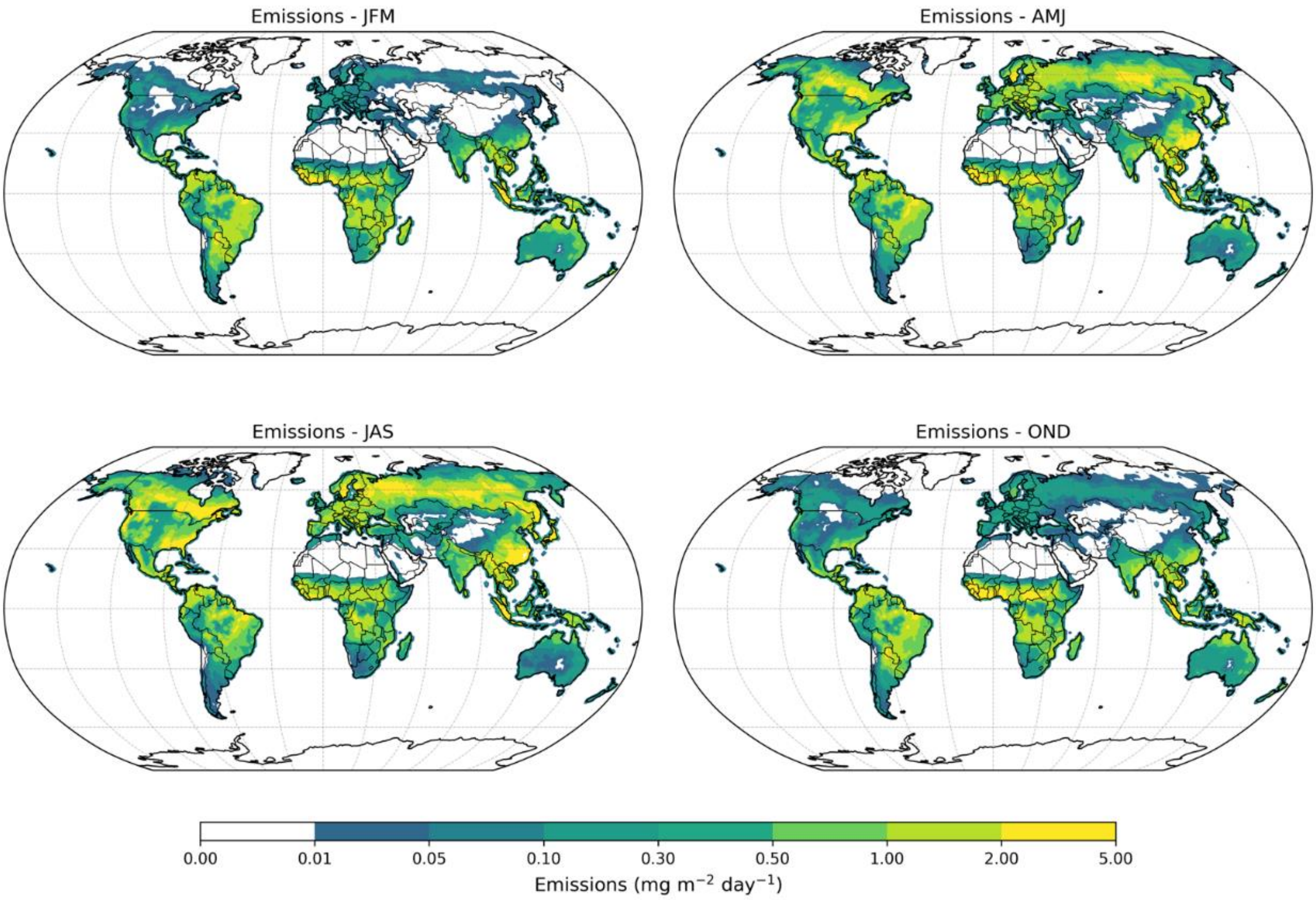

Figure SI 3.1.2.: Seasonal average kaurene emission rates for 2018 where **only 50%** of the vegetation emits kaurene. (JFM: January-February-March; AMJ: April-May-June; JAS: July-August-September; OND: October-November-December.) **Scale 0-5 mg m^{-2} day^{-1}**

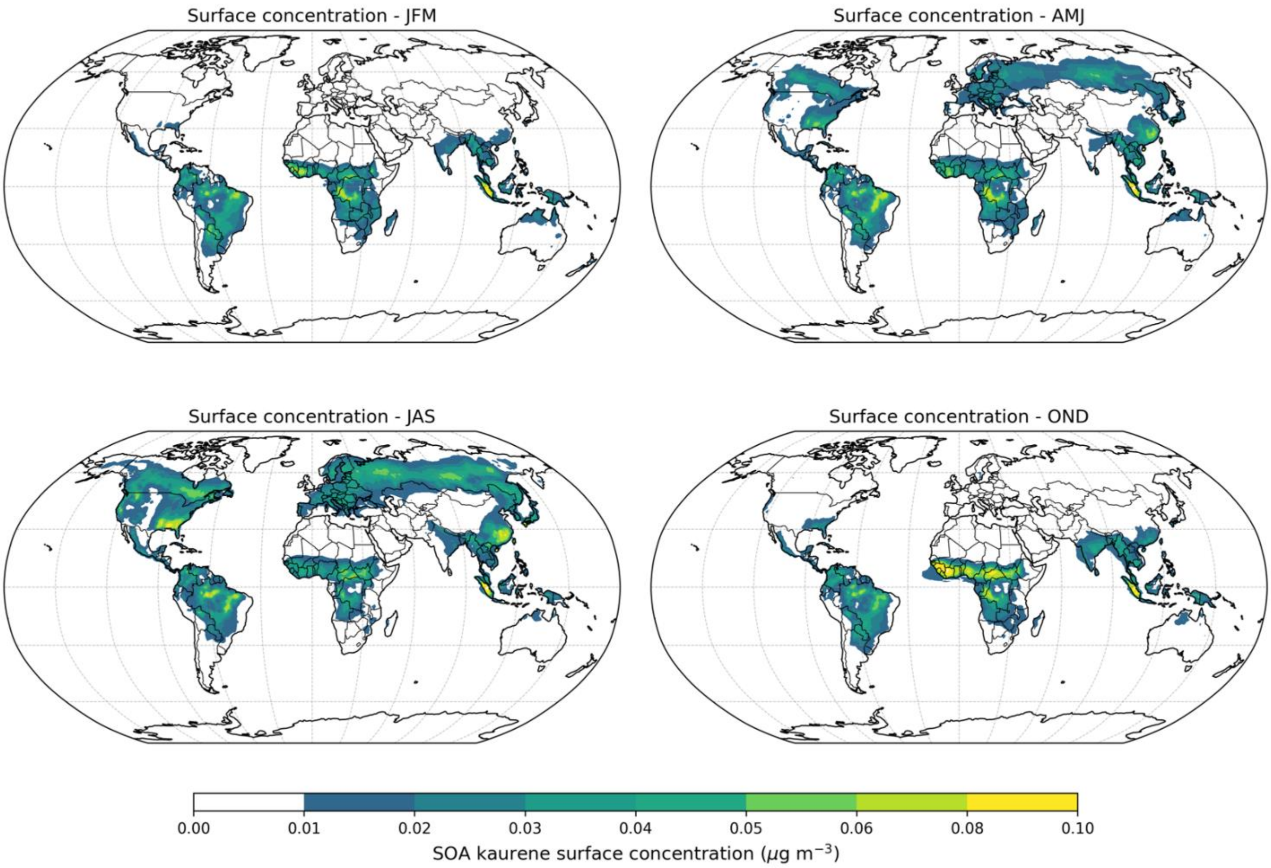

Figure SI 3.1.3: Seasonal average kaurene SOA surface concentration (first model layer – 40m) estimates for 2018 where **only 10%** of the vegetation emits kaurene. (JFM: January-February-March; AMJ: April-May-June; JAS: July-August-September; OND: October-November-December.) **Scale 0-0.1 μg m^{-3}**

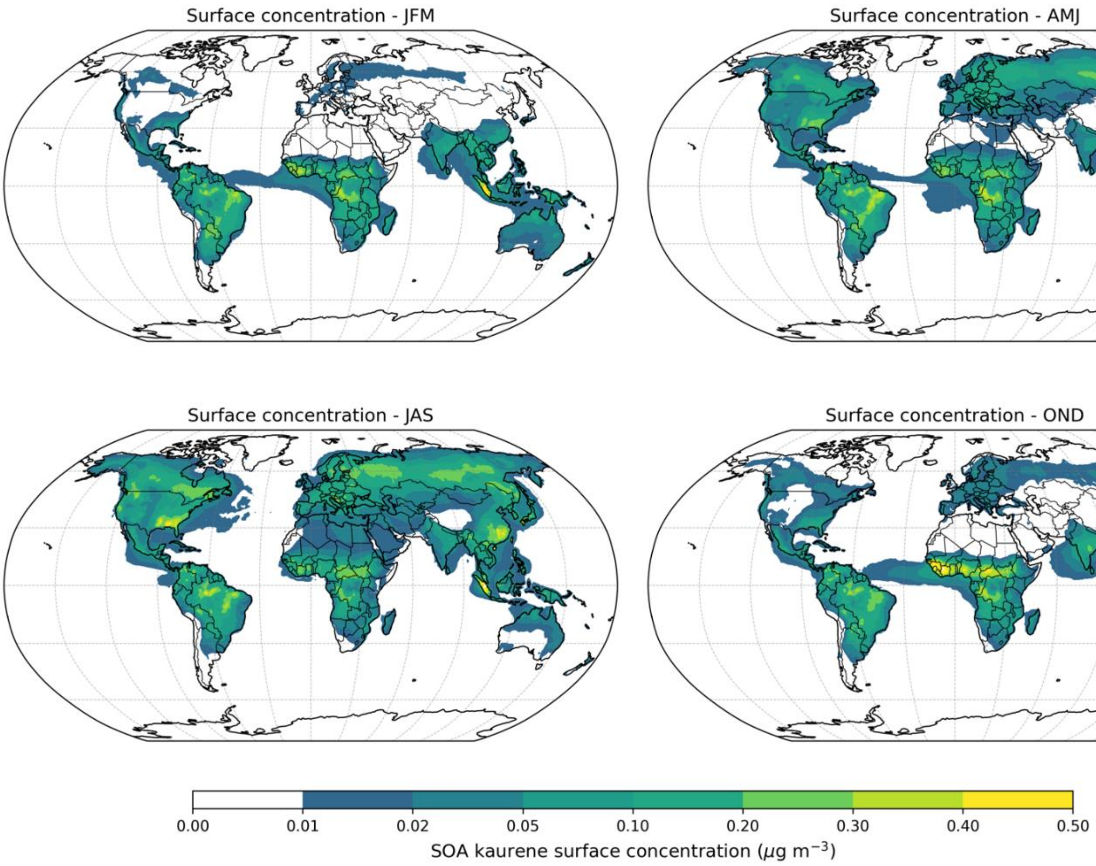

Figure SI 3.1.4: Seasonal average kaurene SOA surface concentration (first model layer – 40m) estimates for 2018 where **only 50%** of the vegetation emits kaurene. (JFM: January-February-March; AMJ: April-May-June; JAS: July-August-September; OND: October-November-December.) **Scale 0-0.5 µg m^{-3}**

3.2. Annual averages of isoprene, monoterpene and sesquiterpenes emission and SOA surface concentrations derived from the model simulation

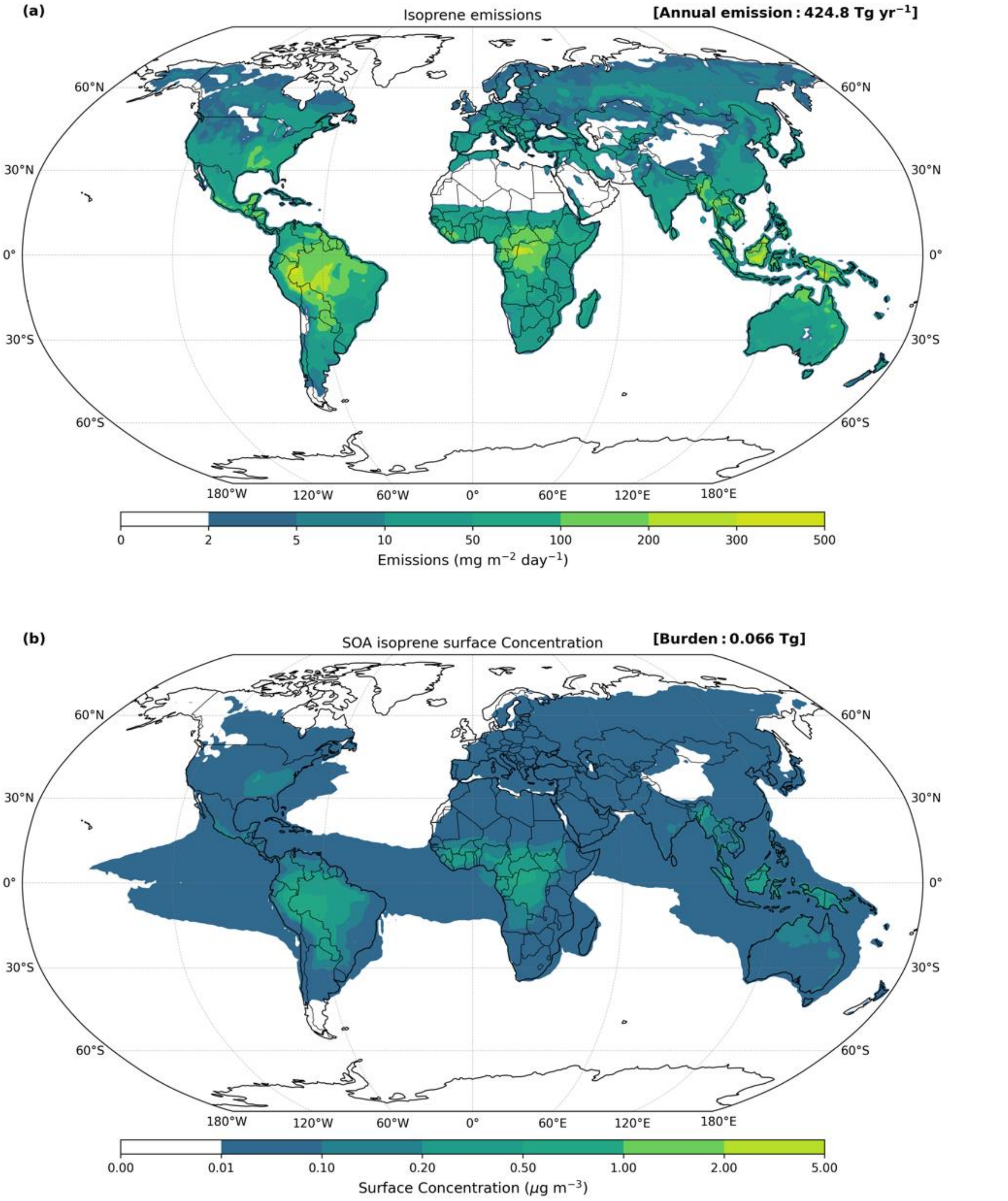

Figure SI 3.2.1: Annual average (a) isoprene emission rates [mg m^{-2} day^{-1}] and (b) SOA isoprene surface concentration [µg m^{-3}] estimates for 2018.

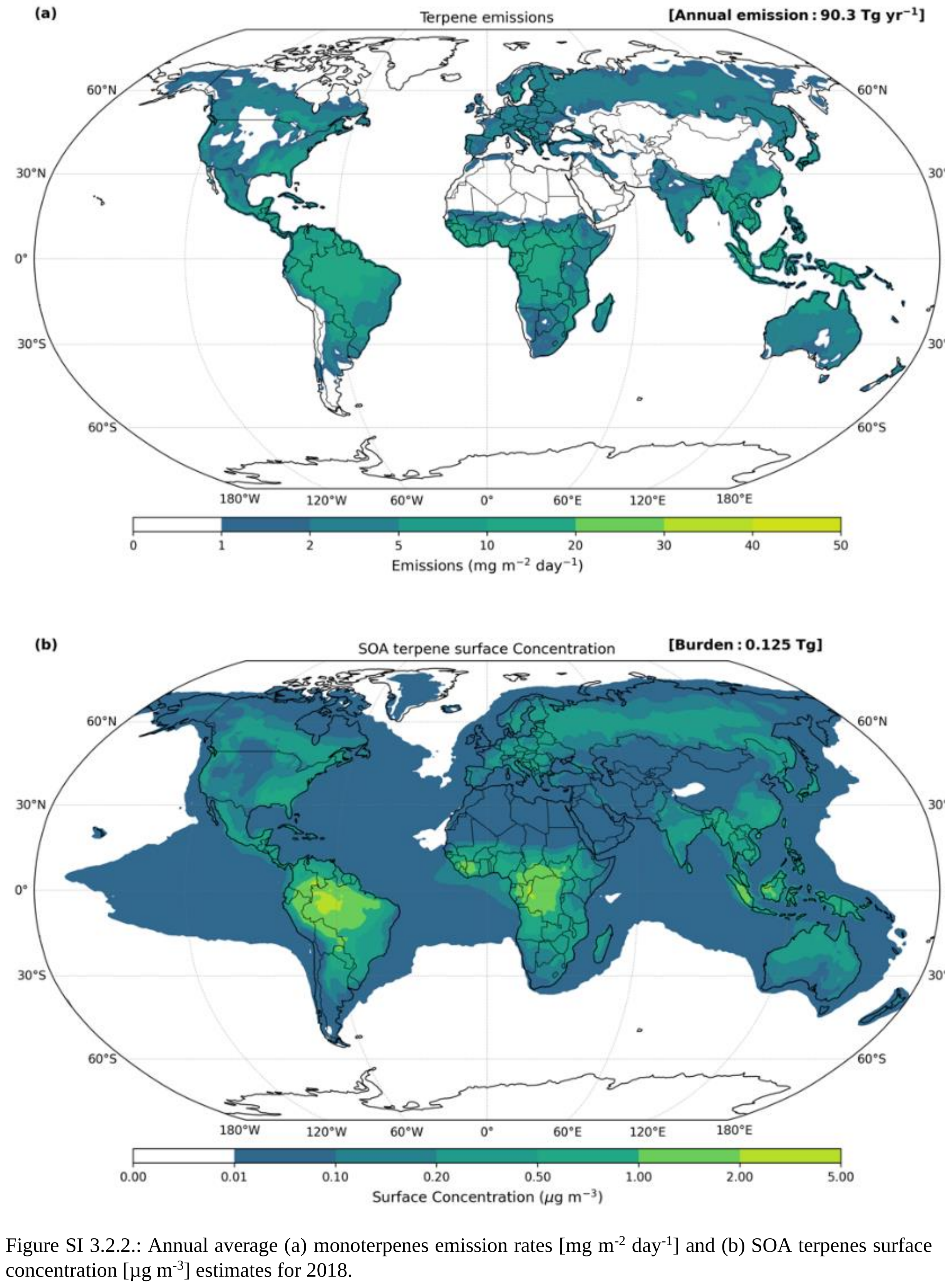

Figure SI 3.2.2.: Annual average (a) monoterpenes emission rates [mg m^{-2} day^{-1}] and (b) SOA terpenes surface concentration [µg m^{-3}] estimates for 2018.

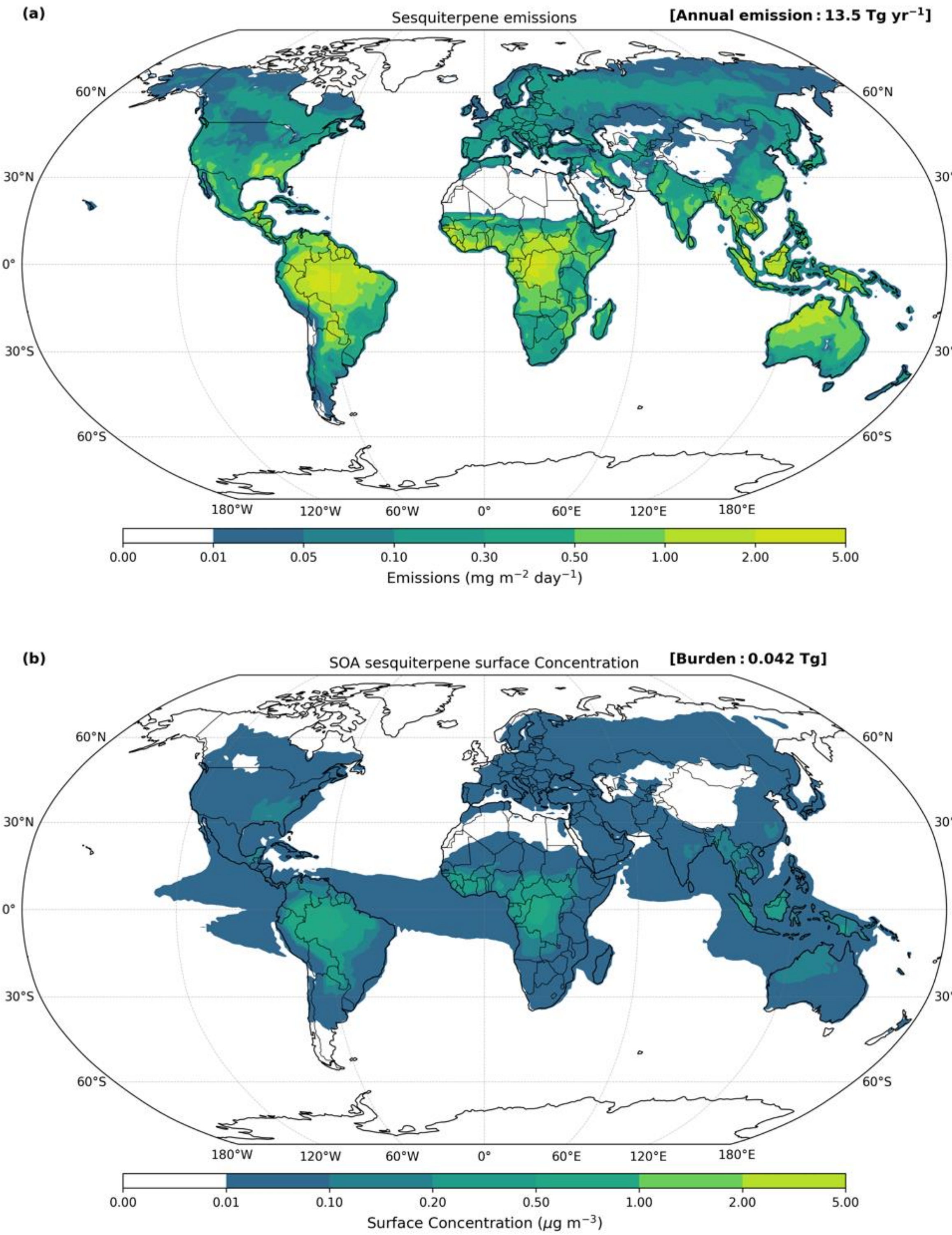

Figure SI 3.2.3.: Annual average (a) sesquiterpenes emission rates [mg m^{-2} day^{-1}] and (b) SOA sesquiterpenes surface concentration [µg m^{-3}] estimates for 2018.

Table S.I.3.: Budget intercomparison with other modelling studies[11–19]

Run	Emissions isoprene ($Tg\ yr^{-1}$)	Emissions kaurene ($Tg\ yr^{-1}$)	Emissions monoterpenes ($Tg\ yr^{-1}$)	Emissions sesquiterpenes ($Tg\ yr^{-1}$)	Burden SOA_isoprene (Tg)	Burden SOA_kaurene (Tg)	Burden SOA_monoterpenes (Tg)	Burden SOA_sesquiterpenes (Tg)
This study	**424.8**	**5.1 - 25.5**	**90.3**	**13.5**	**0.066**	**0.005 - 0.025**	**0.125**	**0.042**
Sindelarova et al. (2022 ESDD)	299-440		82.7	16.6				
Weng et al. (2020 Scientifc DATA) (and references therein)	391 (272-641)		126.6	21.6				
Henrot et al. (2017 GMD) (and references therein)	472 (428-681)		100.5 (37-144)	5.4 (4.8-7.3) β-caryopyllene				
Guenther et al. (2012 GMD)	535 (350-800)		162 (30-144)	17.9				
Heald et al. (2008 JGR)				47				
Henze et al. (2008 ACP)	461		121	14.8	0.45		0.22	0.03
Tsigaridis and Kanakidou (2007 Atmos Environ)	530		155	32%ORVOC; 91.04	0.08		0.69	
Utembe et al. (2011 Atmos Environ)	501		127		0.0078		0.2052	
Khan et al. (2017 JGR) (and references therein)	501		162	29	0.0091-0.0104		0.27-0.37	0.0409-0.043

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