Supplementary Material

A numerical evaluation of global oceanic emissions of α-pinene and isoprene

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1. The emission rates of α-pinene and isoprene from PHYSAT phytoplankton classes

In our work, the emission rates of α-pinene and isoprene for the phytoplankton classes considered by the PHYSAT model (as shown in Table S1) are derived from the work of Yassaa et al. (2008) and Arnold et al. (2009), respectively. The details of the determination of the emission rates of isoprene have been amply described in Arnold et al. (2009). Yassaa et al. (2008) reported the emission rates of monoterpenes from the nine algae species which represent a mean of 16 measurements. In their work, the emission rates for the five diatom species (skeletonema costatum, chaetoceros debilis, chaetoceros neogracilis, fragilariopsis kerguelensis and phaeodactylum tricornutum) are within the range of 0.3-68.1 nmol α-pinene g $[Chl\text{-}a]^{-1}$ day^{-1}. The emission rate for the phaeodactylum tricornutum is 200 times of that for skeletonema costatum. In the present study we assume that the emission rate of α-pinene for diatom class is 43.1 nmol α-pinene g $[Chl\text{-}a]^{-1}$ day^{-1} over the South Ocean and 68.1 nmol α-pinene g $[Chl\text{-}a]^{-1}$ day^{-1} over elsewhere. The uncertainties in the emission rates will affect the 'bottom-up' values but will not influence the 'top-down' values given in this study.

2. The determination of the MAE prefactors

The determination and optimization of the prefactor ξ_{VOC} in equation 1 is important for the evaluation of global oceanic organic source. By finding the best match of GEOS-Chem simulation and the OOMPH measurement, we can determine the value of ξ_{VOC}. Here we use the MAE method to calculate the optimization value of ξ_{VOC}. The MAE method is to minimize the

mean absolute error, thus it provides the closest simulations to the observations.

By employing equation 1 to calculate oceanic organic emissions, we can use GEOS-Chem to simulate the daily mean concentrations of α-pinene and isoprene along the OOMPH ship route. A number of case studies, which use different $\xi_{\alpha-pinene}$ (within the range of 0-3×10^3) and $\xi_{isoprene}$ (within the range of 0-30), have been carried out to obtain the MAEs of simulations in comparison with the observations. Figure S1 presents the dependence of MAE on the values of ξ_{VOC}. The third-order polynomial fit formulas shown in the figure are shown as following:

$$MAE_{\alpha-pinene} = -1.155\times10^{-9}\times\xi^3_{\alpha-pinene} + 1.830\times10^{-5}\times\xi^2_{\alpha-pinene} - 4.465\times10^{-2}\times\xi_{\alpha-pinene} + 7.015\times10 \quad \text{(S1)}$$

$$MAE_{isoprene} = 9.254\times10^{-4}\times\xi^3_{isoprene} + 1.045\times10^{-1}\times\xi^2_{isoprene} - 4.406\xi_{isoprene} + 8.973\times10 \quad \text{(S2)}$$

The values of ξ_{VOC} that give the minimum MAE values for α-pinene and isoprene are 1.4 $\times10^3$ and 17.0, respectively.

By using the MAE prefactors in GEOS-Chem, the mean error (ME), normalized mean error (NME), and mean absolute error (MAE) of the simulated α-pinene and isoprene concentrations are significantly reduced (Table S2).

3. Zonal distribution of oceanic α-pinene and isoprene emissions and representativeness of the OOMPH measurements

Our 'top-down' evaluation of global oceanic emissions of organics mainly relied on the surface concentrations of α-pinene and isoprene which are observed by the OOMPH measurement. Our simulation shows that oceanic emissions of organics appear in both the north and south hemisphere. However, the highest emission areas of α-pinene and isoprene are located over the Southern Ocean region (40ºS-60ºS). For α-pinene, the 20 GgC km^{-1} yr^{-1} oceanic emissions are 2 times larger than the values over tropic and mid-northern latitudes. For isoprene, the differences between the emission over the Southern Ocean and those over tropic and mid-northern latitudes are not as strong as those of α-pinene, however, the Southern Ocean

emission is still ~ 1.5-2 times larger than those over other regions. The high emissions of α-pinene and isoprene in the Southern Ocean regions are as a result of high chlorophyll-a concentrations and wind speeds. As shown in Figure S2, the shipboard measurement covers a large part of the high emission region. Thus, we feel that the OOMPH measurements of oceanic α-pinene could be reasonably representative, although additional measurements of α-pinene over remote oceans are clearly needed.

4. The treatments of monoterpene and isoprene oxidations in GEOS-Chem

In GESO-Chem, the monoterpene oxidation is treated in the code carbon_mod.f, while the isoprene oxidation is treated in SMVGEAR solver. The reaction rates of α-pinene with OH, O_3 and NO_3 are calculated as following:

KO3=56.15e-18×EXP(732.0×(1.0/298.0-1.0/T))

KOH=84.4e-12×EXP(-400.0×(1.0/298.0-1.0/T))

KNO3=6.95e-12×EXP(-490.0×(1.0/298.0-1.0/T))

where T represent temperature in air.

The reaction rates of isoprene in GEOS-Chem with OH, O_3 and NO_3 are calculated as following:

KO3=1.05e-14×EXP(-2000.0/T)

KOH=2.70e-11×EXP(390.0/T)

KNO3=3.03e-12×EXP(-446.0/T)

5. The detailed source and sink information for α-pinene and isoprene based on the bottom-up and top-down approaches on three selected days

We list the details of emission fluxes, chemical loss rates, O_3 concentration, and OH concentration in Table S3. When including the bottom-up oceanic organic emissions, the enhancement of emission flux of isoprene is ~ 20-60 times larger than that of α-pinene. The huge difference between the bottom-up oceanic organic emissions of α-pinene and isoprene is caused

by the different emission rates of the two species. It is very likely that there are other species not surveyed by Yassaa et al. (2008). However, to estimate the fraction of the total plankton biomass represented by the species examined by Yassaa et al. will be difficult due to the lack of data and is out the scope of the present study. By using the top-down approach, both of the emission fluxes of α-pinene and isoprene are increased significantly. The differences of the emission fluxes of α-pinene and isoprene, which are shown in the bottom-up approach, are partially compensated by the prefactors. As shown in Table S3, the emission flux of α-pinene is about 2 times larger than that of isoprene. The difference is as a result of larger molecular weight of α-pinene and slightly short life time of α-pinene over the Southern Ocean.

The simulated daily averaged total chemical loss rates (O_3+OH+NO_3) for α-pinene and isoprene are ~ 0.2-0.44 h^{-1} and ~ 0.17-0.4 h^{-1}, respectively. The total chemical loss rate of α-pinene is a little larger than that of isoprene. It is clear that the chemical loss rate of α-pinene by OH is smaller than that of isoprene. However, the chemical loss rate of α-pinene by O_3 is much larger than that of isoprene and is comparable with those associated with OH over the Southern Ocean. Table S3 indicates that daily averaged concentrations of O_3 and OH are 2.4×10^{11}-4.8×10^{11} molec cm^{-3} and 4×10^{5}-10×10^{5} molec cm^{-3}, respectively. The high O_3 concentration make the chemical loss rate of α-pinene by O_3 become comparable with that by OH. Therefore, the combined chemical loss rate of α-pinene is larger than that of isoprene.

References

Arnold, S. R., et al.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, Atmos. Chem. Phys., 9(4), 1253-1262, 2009.

Yassaa, N., et al.: Evidence for marine production of monoterpenes, Environmental Chemistry, 5(6), 391-401, 2008.

Table S1 Emission rates of α-pinene and isoprene for the phytoplankton classes considered by the PHYSAT model. Data of emission rates of α-pinene is from Yassaa et al. (2008); while data of emission rates of isoprene is from Arnold et al. (2009).

Class	α-pinene emission rate (μmol α-pinene g $[Chl\text{-}a]^{-1}$ day^{-1})	Isoprene emission rate (μmol isoprene g $[Chl\text{-}a]^{-1}$ day^{-1})
Haptophytes	0.0003	1.99
Prochlorococcus	0.2259	9.66
Cyanobacteria	0.0011	7.83
Diatoms (S Ocean)	0.0431	1.21
Diatoms (elsewhere)	0.0681	2.48
Unidentified	0.001	3.13

Table S2 The mean error (ME), normalized mean error (NME), and mean absolute error (MAE) of α-pinene and isoprene concentrations for three different emission scenarios.

	ME: α-pinene	ME: isoprene	NME: α-pinene	NME: isoprene	MAE: α-pinene	MAE: isoprene
NSO	-67.2	-86.1	-99.4%	-88.9%	67.2	86.1
BU	-67.2	-84.7	-99.3%	-87.5%	67.2	84.7
MAE	-22.2	-29.5	-32.9%	-30.5%	38.3	46.9

Table S3 The detailed source and sink information for α-pinene and isoprene based on the bottom-up (BU) and top-down (TD) approaches on three selected days: 01-22-2009 (the second day in Region A), 01-26-2009 (the second day in Region B), and 02-01-2009 (the second day in Region C). The mean model box height at surface layer along the ship route is ~ 126-128 m.

	1-22-2007			1-26-2007			2-01-2007		
	NOS	BU	TD	NOS	BU	TD	NOS	BU	TD
α-pinene emission flux (ng m^{-2} day^{-1})	0.0E+00	6.0E+01	2.1E+05	0.0E+00	1.9E+02	1.6E+06	0.0E+00	1.8E+02	1.9E+05
isoprene emission flux (ng m^{-2} day^{-1})	0.0E+00	3.7E+03	1.9E+05	0.0E+00	7.8E+03	8.9E+05	0.0E+00	3.5E+03	4.9E+04
α-pinene loss rate by O_3 (h^{-1})	4.6E-02	4.6E-02	4.6E-02	7.9E-02	7.9E-02	7.6E-02	9.0E-02	9.0E-02	8.6E-02
α-pinene loss rate by OH (h^{-1})	2.2E-01	2.2E-01	1.7E-01	2.8E-01	2.8E-01	1.3E-01	3.2E-01	3.2E-01	2.2E-01
α-pinene loss rate by NO_3 (h^{-1})	1.6E-04	1.6E-04	5.5E-05	1.8E-03	1.8E-03	8.4E-04	2.4E-02	2.4E-02	1.4E-02
chemical loss rate of α-pinene (h^{-1})	2.7E-01	2.7E-01	2.1E-01	3.6E-01	3.6E-01	2.0E-01	4.4E-01	4.4E-01	3.2E-01
isoprene loss rate by O_3 (h^{-1})	9.4E-03	9.4E-03	9.4E-03	1.5E-02	1.5E-02	1.4E-02	1.8E-02	1.8E-02	1.7E-02
isoprene loss rate by OH (h^{-1})	2.6E-01	2.6E-01	2.0E-01	3.3E-01	3.3E-01	1.5E-01	3.8E-01	3.8E-01	2.6E-01
isoprene loss rate by NO_3 (h^{-1})	1.5E-05	1.5E-05	5.0E-06	1.6E-04	1.5E-04	7.3E-05	2.1E-03	2.1E-03	1.3E-03
chemical loss rate of isoprene (h^{-1})	2.7E-01	2.7E-01	2.1E-01	3.5E-01	3.4E-01	1.7E-01	4.0E-01	4.0E-01	2.8E-01
O_3 concentration (molec cm^{-3})	2.4E+11	2.4E+11	2.4E+11	4.4E+11	4.4E+11	4.2E+11	4.8E+11	4.8E+11	4.6E+11
OH concentration (molec cm^{-3})	7.1E+05	7.1E+05	5.4E+05	8.7E+05	8.6E+05	4.0E+05	1.0E+06	1.0E+06	6.9E+05

Figure Captions:

Figure S1. The distributions of Mean Absolute Error (MAE) of the 31 cases which use different prefactors: (a) α-pinene, (b) isoprene. The solid line is the third-order polynomial fit of the MAE distribution.

Figure S2. Zonal distribution of total oceanic organic emissions: (a) α-pinene, (b) isoprene.

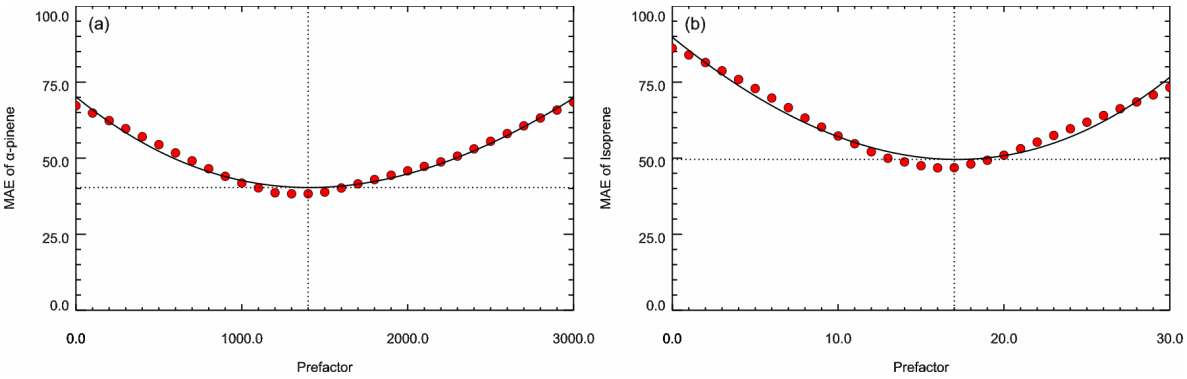

Figure S1.

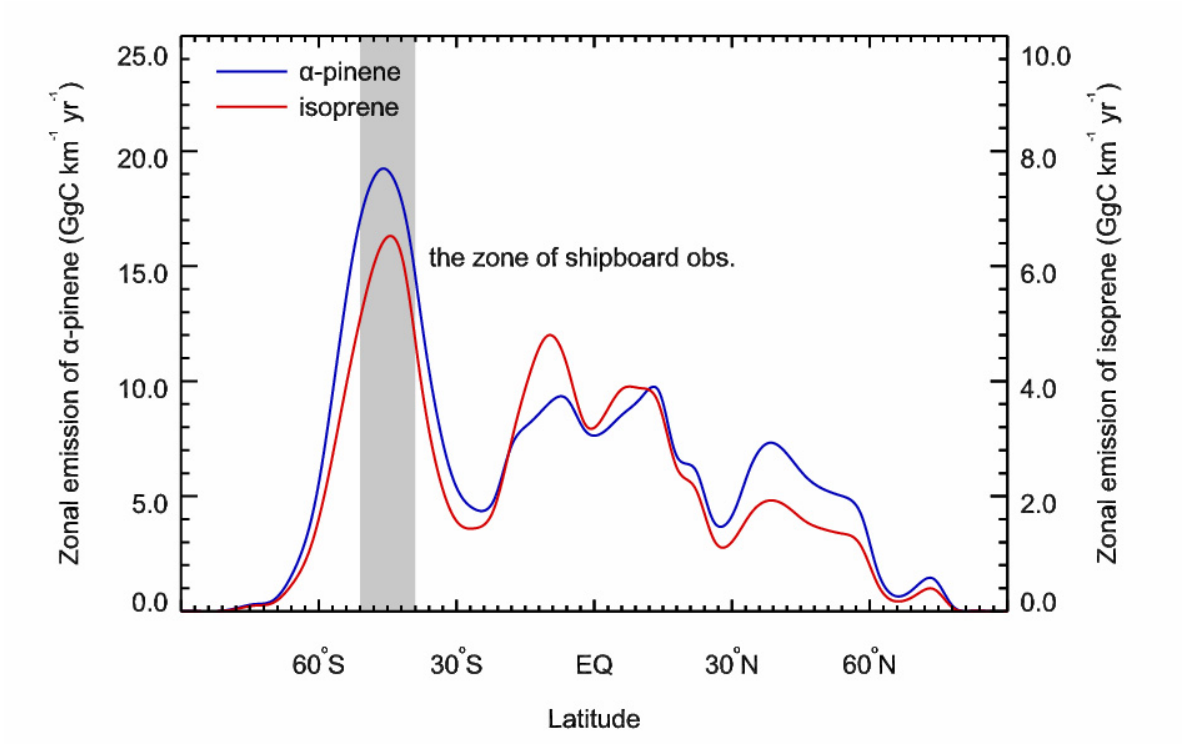

Figure S2.