Supplementary Material

for the manuscript acp-2009-537 '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 $2\times10^2 \sim 6\times10^3$) and $\xi_{isoprene}$ (within the range of 0.4 ~ 12), 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:

$$MAE_{\alpha-pinene} = -2.608\times10^{-10}\times\xi^3_{\alpha-pinene} + 7.072\times10^{-6}\times\xi^2_{\alpha-pinene} - 3.048\times10^{-2}\times\xi_{\alpha-pinene} + 7.224\times10 \quad \text{(S1)}$$

$$MAE_{isoprene} = -2.702\times10^{-2}\times\xi^3_{isoprene} + 1.691\times\xi^2_{isoprene} - 1.733\times10\times\xi_{isoprene} + 9.457\times10 \quad \text{(S2)}$$

The values of ξ_{VOC} that give the minimum MAE values for α-pinene and isoprene are 2.5 $\times10^3$ and 6.0, 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 30 GgC km^{-1} yr^{-1} oceanic emissions are 3 times higher 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 higher 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.

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	-67.4	-87.2	-99.7%	-90.0%	67.4	87.2
BU	-67.4	-82.1	-99.6%	-84.8%	67.4	82.1
MAE	-17.6	-25.4	-26.1%	-26.2%	35.8	43.9

Figure Captions:

Figure S1. The distributions of Mean Absolute Error (MAE) of the 30 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.

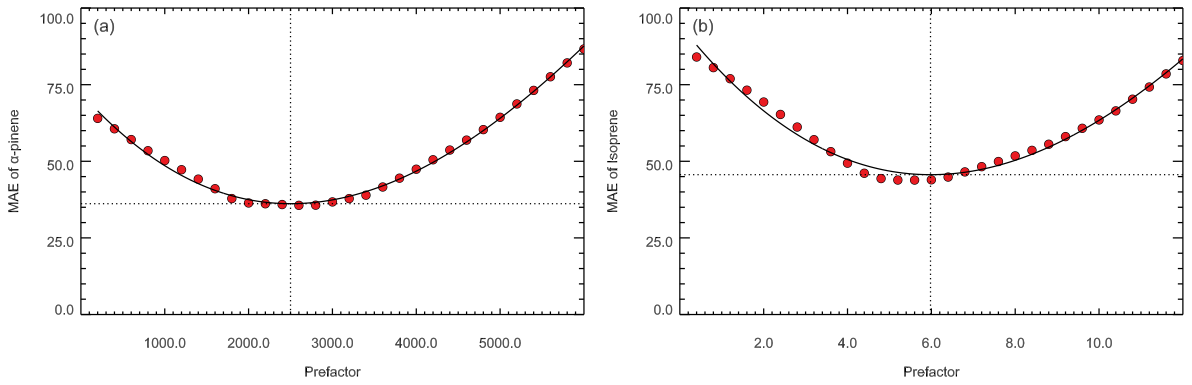

Figure S1.

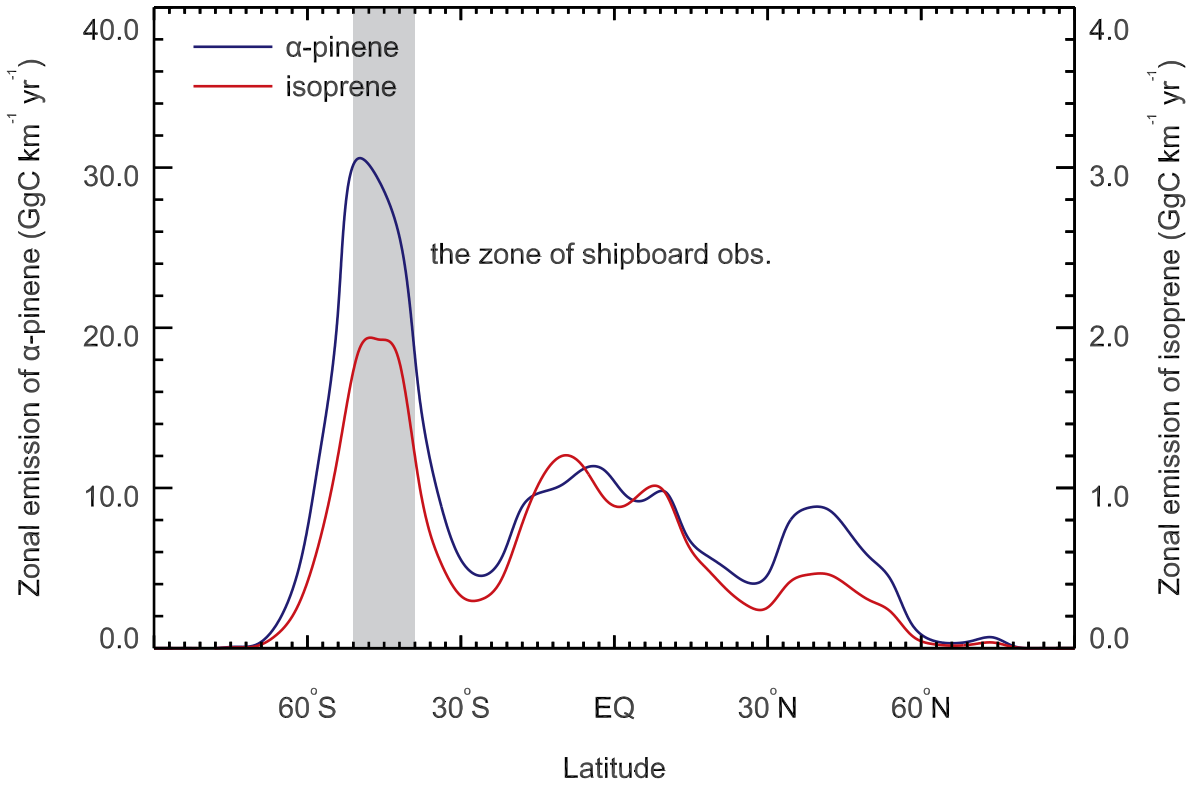

Figure S2.