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

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Abstract

A numerical evaluation of global oceanic emissions of α-pinene and isoprene based on both "bottom-up" and "top-down" methods is presented. As far as we know, this is the first quantification of global oceanic emission of α-pinene. We infer that the global "bottom-up" oceanic emissions of α-pinene and isoprene are 0.013 Tg C yr^{-1} and 0.32 Tg C yr^{-1}, respectively. By constraining global chemistry model simulations with the shipboard measurement of Organics over the Ocean Modifying Particles in both Hemispheres summer cruise, we derived the global "top-down" oceanic α-pinene source of 35.1 Tg C yr^{-1} and isoprene source of 2.5 Tg C yr^{-1}. The global oceanic α-pinene source and its impact on organic aerosol formation is significant based on "top-down" method, but is negligible based on "bottom-up" approach. Our research highlights the importance to carry out further research (especially measurements) to resolve the large offset in the derived oceanic organic emission based on two different approaches.

1 Introduction

Satellite remote sensing has indicated high aerosol optical depth over the Southern Ocean (Kaufman et al., 2002). Because of the potential impact of these aerosols on the Antarctic and Southern Ocean multidecadal climate changes via direct and indirect radiative forcing (Mayewski et al., 2009), the chemical composition and formation mechanism of aerosols over this region has been one of the most intriguing questions in atmospheric chemistry and climate studies. Sea salt, dimethylsulfide (DMS), and primary and secondary organic carbon have all been suggested as species that may have significant contribution to the aerosol zone over the Southern Ocean (Ceburnis et al., 2008; Gabric et al., 2005; Meskhidze and Nenes, 2006; Murphy et al., 1998; O'Dowd et al., 2008).

Global modeling also indicated the missing of large organic aerosol source(s) in the troposphere (Gantt et al., 2009; Heald et al., 2005, 2006; Roelofs, 2008; Spracklen et al., 2008), although the exact species and sources remain controversial. Heald et al. (2006) introduced in GEOS-Chem a 27 Tg C yr^{-1} marine OC aerosol source by convolving the sea salt aerosol source with the seasonal variation of marine primary productivity, and scaling globally this source to match mean OC aerosol measurements over the remote oceans. Spracklen et al. (2008) derived an empirical relation between SeaWiFS chlorophyll-a concentration and the oceanic OC emission flux, and showed that 8 Tg C yr^{-1} of global oceanic OC emissions (primary plus secondary) are needed to match the OC aerosol concentrations observed at three oceanic surface sites. Roelofs (2008) estimated that globally, about 75 Tg C yr^{-1} of organic matter from marine origin enters the aerosol phase, with comparable contributions from primary emissions (35$\sim$50 Tg C yr^{-1}) and secondary organic aerosol formation (25$\sim$40 Tg C yr^{-1}). Isoprene was suggested as the most possible source for the marine SOA (Meskhidze and Nenes, 2006; Roelofs, 2008). However, in-situ observation, satellite measurements and model simulation inferred that the total annual mean oceanic isoprene emission is only $\sim$0.1–1.9 Tg yr^{-1} (Arnold et al., 2009; Broadgate et al., 1997; Gantt et al., 2009; Palmer and Shaw, 2005), too low to explain the WSOC observed over the ocean.

Recent shipboard measurement of Organics over the Ocean Modifying Particles in both Hemispheres (OOMPH) summer cruise reported that both marine α-pinene and isoprene, along their route from Cape Town of South Africa to Punta Arenas of Chile, can reach up to $\sim$150 pptv (Yassaa et al., 2008). The data was obtained by analyzing the cartridges from shipborne samples using an on-line gas chromatograph-mass spectrometer (GC-MS) analysis system, with the detection limits of isoprene and α-pinene ranging from 1 to 5 pptv, and the total uncertainties of $\sim$10–15% (Yassaa et al., 2008). Yassaa et al. (2008) also incubated several phytoplankton cultures and measured their monoterpene emission rates in the laboratory. The shipboard measurements and laboratory incubation experiments of Yassaa et al. (2008) provided the first evidence of marine production of α-pinene. Compared to isoprene, α-pinene has much higher reactivity and SOA yield. A substantial concentration of α-pinene over the ocean is a strong indication of significant oceanic source. As far as we know, the global evaluation of oceanic α-pinene emission has not been studied before.

The main objective of this study is to derive global oceanic α-pinene source strength based on both "top-down" and "bottom-up" methods. For comparison, oceanic isoprene emission is also derived in a similar way. The possible impact of these oceanic emissions on SOA formation and chemistry over the Southern Ocean is also discussed.

2 Treatment of oceanic organic emissions

Previous studies indicated a correlation between the seasonal cycle of OC measured at surface sites and oceanic chlorophyll-*a* concentration ([Chl-*a*]) observed from satellite. Two different methods have been widely used to estimate oceanic OC emissions: one is the "bottom-up" method which deduces the sea-to-air emissions based on the emission flux measurements (Arnold et al., 2009; Gantt et al., 2009); the other is "top-down" method which infers the key parameters via matching final simulations with observations (Arnold et al., 2009; Heald et al., 2006; Spracklen et al., 2008). Spracklen et al. (2008) obtained the oceanic OC emission through scaling [Chl-*a*] by an emission factor A=3.2 ng C m^{-2} s^{-1}/mg [Chl-*a*] m^{-3}. Arnold et al. (2009) inferred a mean "bottom-up" oceanic isoprene emission of 0.31±0.08 Tg yr^{-1}, and a "top-down" oceanic isoprene source estimate of 1.9 Tg yr^{-1}. Gantt et al. (2009) developed a new physically-based parameterization for the emission of isoprene and primary organic matter that takes into account the effect of [Chl-*a*], solar radiation, total water depth, and wind speed on emission.

In this study, we calculated the "bottom-up" emission flux (F_{VOC}, VOC=α-pinene, isoprene) as (Arnold et al., 2009),

$$F_{\mathrm{VOC}} = R_{\mathrm{VOC}}\,[\text{Chl-}a]\,D_{\mathrm{ML}} \tag{1}$$

where R_{VOC} is the emission rate of VOC (Arnold et al., 2009; Yassaa et al., 2008), which is determined by the measurements and experiments for the phytoplankton classes considered by the PHYSAT model (Alvain et al., 2008). [Chl-*a*] is the monthly mean oceanic chlorophyll-a concentration at model resolution which is regrided from the merged MODIS Aqua and SeaWiFS chlorophyll-a Level-3 products with 9 km×9 km resolution, and D_{ML} is the climatic monthly mean mixed layer depth (de Boyer et al., 2004).

Based on the "top-down" method, we calculate oceanic emission of α-pinene and isoprene with the following formula, which parameterizes emission flux (F_{VOC}, VOC=α-pinene, isoprene) as a function of [Chl-*a*], D_{ML}, R_{VOC}, effective solar radiation rate (R_{sun}), surface wind velocity at 10 m ($W_{10\,\mathrm{m}}$), and Schmidt number (Sc).

$$F_{\mathrm{VOC}}\left(\text{in kg m}^{-2}\,\text{s}^{-1}\right) = \xi_{\mathrm{VOC}}\,[\text{Chl-}a]\,D_{\mathrm{ML}}R_{\mathrm{VOC}}R_{\mathrm{sun}}k_{600}\sqrt{\mathrm{Sc}_{\mathrm{CO_2}}/\mathrm{Sc}_{\mathrm{VOC}}} \qquad (2)$$

where ξ_{VOC} is a prefactor that is to be determined by matching modeled VOC concentrations with those measured (the details of how to obtain the prefactor are described in supplementary material, http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf). R_{sun} depends on solar altitude, optical depth of cloud and aerosol, and surface albedo. The exact simulation of R_{sun} needs a full radiative transfer model. In this study, we only consider the spatial and temporal impact of solar altitude. k_{600} is the gas transfer velocity normalized to a Schmidt number (Sc) of 600 which is calculated based on the fitted formula of Nightingale et al. (2000),

$$k_{600} = 0.24W_{10\,\mathrm{m}}^2 + 0.061W_{10\,\mathrm{m}} \qquad (3)$$

where $W_{10\,\mathrm{m}}$ is the surface wind speed extracted from GEOS-5 metrological field. The Schmidt number, Sc, is defined as the kinematic viscosity of water divided by diffusion coefficient of the gas. In the present study, $\mathrm{Sc}_{\mathrm{CO_2}}$=600, while $\mathrm{Sc}_{\mathrm{VOC}}$ is calculated via the third-order polynomial fit of sea surface temperature (SST) (Palmer and Shaw, 2005; Wanninkhof, 1992).

3 Oceanic α-pinene and isoprene emissions and the associated impact on SOA concentrations

The global model employed in this study is GEOS-Chem v8-01-03 (http://www-as.harvard.edu/chemistry/trop/geos), with an advanced particle microphysics model (APM) incorporated to treat size-resolved microphysics, dry deposition, and wet scavenging for aerosols (for details, see Yu and Luo, 2009). The updated GEOS-Chem is driven by the assimilated meteorological data from the NASA Goddard Earth Observing System 5 (GEOS-5) at 4°×5° horizontal resolutions. With GEOS-Chem and Eq. (1), we find that the global "bottom-up" oceanic emission of α-pinene and isoprene in the year 2006 are 0.013 Tg C yr^{-1} and 0.32 Tg C yr^{-1}, respectively. Our calculated value of global oceanic isoprene emission is close to that of Arnold et al. (2009) (0.31 Tg yr^{-1} for year 2000), based on the similar approach. Because of the much lower emission rates (R_{VOC}) of α-pinene based on laboratory measurements (see Table S1 in supplementary material, http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf), the global "bottom-up" oceanic emission of α-pinene is a factor of ~25 smaller than that of isoprene.

Due to their high reactivity and thus short lifetime, the concentrations of α-pinene and isoprene over the oceans are generally negligible (<1 pptv) in the absence of oceanic source. The observed high concentrations (up to ~150 pptv) of α-pinene and isoprene over the Southern Ocean, as reported by Yassaa et al. (2008), strongly suggest an oceanic source of these species. One logical question to ask is: can the "bottom-up" emission fluxes calculated above account for the observed α-pinene and isoprene over the Southern Ocean? If not, what is the amount of the emission needed to maintain the observed concentrations (i.e., "top-down" emission values)? To answer these questions, we employ GEOS-Chem, which includes full organic chemistry and takes into account transport and deposition processes.

Figure 1a shows a comparison of simulated α-pinene and isoprene concentrations for different emission scenarios with those measured along the ship route reported in

Yassaa et al. (2008). A scatter diagram of observed and simulated daily mean α-pinene and isoprene concentrations during the same period is shown in Fig. 1b. The mean error (ME), normalized mean error (NME), and mean absolute error (MAE) of the simulated α-pinene and isoprene concentrations, with respect to the observed values, are summarized in Table 1. Yassaa et al. (2008) divided the observations into 3 regions: the low chlorophyll-a regions (region A) from 20°22′ E, 35°49′ S to 11°17′ W, 43°18′ S; the distant bloom area (region B) from 11°17′ W, 43°18′ S to 48°42′ W, 41°51′ S; and the in-situ bloom region (region C) from 48°42′ W, 41°51′ S to 65°47′ W, 47°54′ S. It is clear that the model without oceanic organic emissions (NOS) cannot reproduce the value of the shipboard measurements, especially over remote ocean regions. The "bottom-up" emissions (BU) does not present noticeable changes in α-pinene concentrations, while the daily average isoprene concentration enhances by ~5 pptv, still much lower than the observed values. With BU emissions, the mean error, normalized mean error, and mean absolute error of α-pinene and isoprene are in the ranges of 60~90 pptv, 80~100% and 60~90 pptv, respectively (Table 1).

To account for the observed α-pinene and isoprene concentrations along the ship route, we calculated the emission rates based on Eq. (2) and determined the prefactors by minimizing the MAE of simulated values (see supplementary material for details, http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf). By using "top-down" MAE prefactor emissions, all of ME, NME and MAE have been significantly reduced. In MAE prefactor case, the ME of α-pinene and isoprene are only −17.6 and −25.4 pptv, respectively; while the NME of α-pinene and isoprene are reduced to −26.1 and −26.2%, respectively. The MAE of α-pinene and isoprene are 35.8 and 43.9 pptv, respectively. The deviation is likely a result of difference in spatiotemporal resolution and the uncertainties associated with chlorophyll-a concentration, phytoplankton functional types, emission rates of different phytoplankton types, oceanic organic emission scheme, and organic chemistry.

The comparisons between GEOS-Chem simulations and the OOMPH measurements indicate that the “bottom-up” oceanic emission can hardly explain the observed α-pinene and isoprene along the ship route. In contrast, with the “top-down” oceanic organic emissions, model simulations are able to capture the major trend of the shipboard measurement along the route.

To assess the global source of oceanic organics and the associated impact on SOA abundance, we carried out two case studies: one without oceanic organic emissions (NOS), and the other considering the “top-down” oceanic α-pinene and isoprene emissions (based on Eq. (2) with MAE prefactors $\xi_{\alpha\text{-pinene}}=2.5\times10^3$ and $\xi_{\text{isoprene}}=6.0$). The MAE prefactors are used because they provide simulated results closest to the OOMPH measurements. Figure 2 shows the horizontal distributions of annual mean concentrations (for the year 2006) of α-pinene and isoprene in the surface layer for the two cases. The global terrestrial emission of α-pinene and isoprene in the year 2006 are 127 Tg C yr^{-1} and 602 Tg C yr^{-1}, respectively. However, because of their short atmospheric lifetime, the high surface concentrations of α-pinene and isoprene, which can reach up to 300 and 5000 pptv, are mainly confined to land. Without oceanic emissions, the surface concentrations of α-pinene and isoprene over most oceans are near 0 (Fig. 2a and b). It is clear that the transport from terrestrial sources cannot account for the abundance of α-pinene and isoprene observed in the remote marine boundary layer as reported in Yassaa et al. (2008). After considering oceanic emissions with source strengths that give reasonable agreement with shipboard measurement (Fig. 1), the annual mean surface concentrations of α-pinene and isoprene over the oceans are substantially enhanced, especially in middle latitude marine regions. As a result of large emissions associated with high chlorophyll-*a* concentrations and wind speeds, α-pinene and isoprene concentrations in the Southern Ocean regions (40° S∼60° S) are significantly enhanced and can reach up to 100 pptv.

Based on Eq. (2) and MAE prefactors, the global “top-down” oceanic emissions of α-pinene and isoprene are 35.1 and 2.5 Tg C yr^{-1}, respectively. The 35.1 Tg C yr^{-1} “top-down” oceanic α-pinene emission derived in this study, which is about a quarter of the total terrestrial sources (127 Tg C yr^{-1}), is significant compared with the terrestrial source. Figure 2c indicates that α-pinene concentration over the Southern Ocean is comparable to the values over North America, Europe, and East Asia. The 2.5 Tg C yr^{-1} "top-down" oceanic isoprene emission derived in this study by constraining the model simulations with Yassaa et al. (2008)'s shipboard measurement is slightly higher than the Arnold et al. (2009)'s "top-down" estimation of 1.9 Tg yr^{-1}, which was derived from a different set of isoprene observations over remote oceans.

Apparently, there exists a huge difference in the derived α-pinene and isoprene emissions from "bottom-up" and "top-down" methods. The offset for α-pinene (a factor of $\sim$2700) is much larger than that for isoprene (a factor of $\sim$8). Arnold et al. (2009) showed that oceanic isoprene emission derived from "top-down" method is a factor of $\sim$6 higher than that based on "bottom-up" calculation. Our study, based on a different set of isoprene measurements over remote oceans, confirms the existence of such offset for isoprene. The much larger offset for α-pinene is associated with the much lower α-pinene emission potentials of major phytoplankton types based on laboratory flux measurements (Table S1, supplementary material, http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf) and much higher oceanic α-pinene flux needed to account for the observed α-pinene concentrations over the Southern Ocean. As discussed in Arnold et al. (2008), the possible reasons of the offset include incomplete understanding of the in-situ phytoplankton communities and their range of emission potentials as well as the uncertainties in the "top-down" approach.

The offset by a factor of 2700 in the derived oceanic α-pinene emissions from "bottom-up" and "top-down" methods is obviously significant. However, it is difficult to determine which emission source is more realistic, and further research (especially in-situ measurements) is needed to resolve the differences. As we have shown in Fig. 1, there is no way that the "bottom-up" oceanic emission can explain the observed α-pinene and isoprene along the ship route.

It should be emphasized that the α-pinene concentration data, which the current study relied on, is spatially and temporally limited. As far as we know, no other remote marine monoterpene observations exist, except those reported in Yassaa et al. (2008). Nevertheless, we would also like to point out that OOMPH measurements covered a reasonably wide area in the southern ocean region (from Cape Town, South Africa to Punta Arenas, Chile), and the measurements were taken during a period of more than two weeks coinciding with the annual phytoplankton maximum in the region. As shown in Fig. 2, around 50% of annual oceanic α-pinene emission (i.e., ~35 Tg C/yr) is from the southern ocean region (~30° S–75° S) during the phytoplankton active season (also see Fig. S2 in the supplementary material, http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf). Thus, we feel that OOMPH measurement of oceanic α-pinene could be reasonably representative, although additional measurements of α-pinene over remote oceans are clearly needed.

α-pinene is well recognized to be an important precursor of SOA. The SOA yielding of α-pinene photo-oxidation products is much higher than that of isoprene. Experiment studies implicated that SOA mass yield of α-pinene (32%) is 16 times higher than that of isoprene (2%) (Lee et al., 2006). The potential importance of oceanic α-pinene emission can be assessed with GEOS-Chem, which includes the up-to-date schemes of the organic chemistry (Liao et al., 2007). In GEOS-Chem, SOG1 and SOA1 represent the secondary organic gas and aerosol yielding from α-pinene and β-pinene group, while SOG4 and SOA4 represent the secondary organic gas and aerosol yielding from isoprene group. Figure 3 presents the zonally-averaged relative and absolute differences in SOG4+SOA4 and SOG1+SOA1 between the MAE case and the NOS case. during the summer season (DJF) in the Southern Hemisphere. The zonally-averaged SOG1+SOA1 enhanced by more than 120 ng C m^{-3} within the latitude range of 40° S~60° S (Fig. 3b), with the corresponding relative change in the boundary layer reaches above 200% (Fig. 3a). The enhancement of SOG4+SOA4 is less than 3 ng C m^{-3} (Fig. 3d), and its relative change is about 10% (Fig. 3c). Arnold et al. (2009) suggested that the contribution of isoprene to total OC measured at 3 remote sites is ~1%. Our research also indicates that isoprene has a small contribution to the formation of SOA. Our simulations indicate that α-pinene from oceans, derived from “top-down” method, may significantly contribute to the formations of SOA over the Southern Ocean during the summer season. The secondary organics, which are yielded from α-pinene, may partially explain the observed seasonal variations of organic mass and the soluble fraction over coast and remote oceans (Ceburnis et al., 2008; Spracklen et al., 2008).

4 Summary and discussion

In-situ measurements indicate significant amounts of organic carbon aerosols within marine boundary layer, especially in the regions with enhanced oceanic biological activity. A substantial fraction of these organic carbon aerosols are water soluble (WSOC), but the source of these WSOC remains to be established.

In this study, we seek to quantify the oceanic emissions of α-pinene and isoprene using both “bottom-up” and “top-down” methods. An oceanic organics emission parameterization, which considers the influences of solar radiation, sea surface wind speed, and sea surface temperature, has been employed here to simulate the “top-down” oceanic emission of α-pinene and isoprene. By constraining global chemistry model simulations with shipboard measurements of α-pinene and isoprene concentrations over the Southern Ocean region, we derive a “top-down” global oceanic α-pinene source of 35.1 Tg C yr^{-1} and isoprene source of 2.5 Tg C yr^{-1}. In contrast, our calculated “bottom-up” global oceanic emissions of α-pinene and isoprene are 0.013 Tg C yr^{-1} and 0.32 Tg C yr^{-1}, respectively. Our derived “bottom-up” and “top-down” oceanic isoprene emissions are close to those in previous studies. The global oceanic α-pinene source, quantified for the first time in this study, is significant (compared with the terrestrial source) based on “top-down” method, but is negligible based on “bottom-up” approach. The large offset in the derived oceanic organic emissions (especially for α-pinene) is likely due to the incomplete understanding of the in-situ phytoplankton communities and their range of emission potentials as well as the uncertainties in the “top-down” approach. At this point, it is hard to tell which one is more close to the real values, and further research (especially measurements) is urgently needed to resolve the difference.

Our study indicates that the contribution of oceanic isoprene source, either based on “top-down” or “bottom-up” values, to the formation of oceanic secondary organics appears to be small. While the oceanic α-pinene emission based on the “bottom-up” value has little effect on organic aerosol formation, our simulation shows that oceanic α-pinene emission derived from the “top-down” approach can increase the zonally-averaged secondary organics concentration by up to 200% in the lower troposphere of the Southern Hemisphere (40° S–90° S) during the austral summer season and thus may contribute to the seasonal variations of OC mass and the soluble fraction observed over coast and remote oceans.

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Table 1. 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

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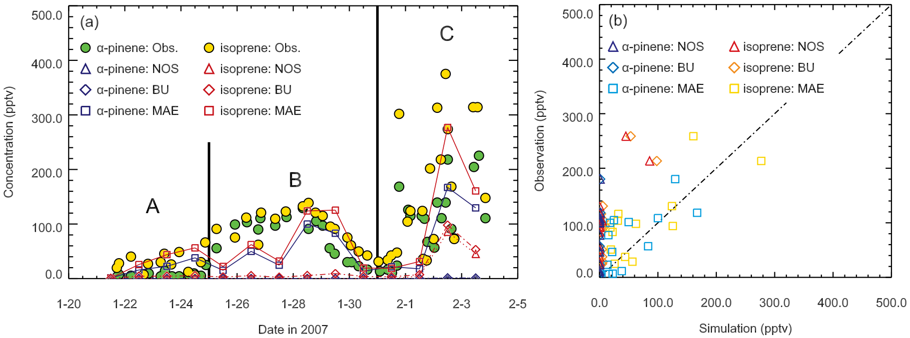
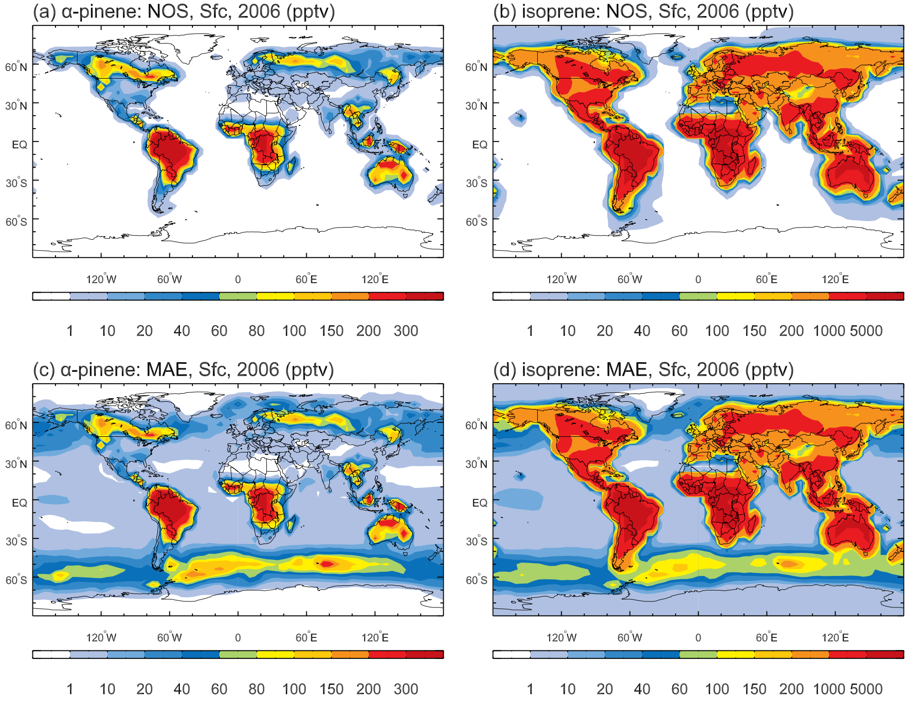


Fig. 1. **(a)** A comparison of observed and simulated *α*-pinene and isoprene concentrations along the route of shipboard measurement (22 January 2007∼4 February 2007) during the OOMPH summer cruise reported in Yassaa et al. (2008). **(b)** A scatter diagram of observed versus simulated *α*-pinene and isoprene concentrations. Obs: the OOMPH measurements; NOS: no oceanic organic emissions; BU: "bottom-up" emissions; MAE: "top-down" MAE prefactor emissions. Definitions of MAE prefactors are given in supplementary material (http://www.atmos-chem-phys-discuss.net/9/20721/2009/acpd-9-20721-2009-supplement.pdf).


(a) α-pinene: NOS, Sfc, 2006 (pptv)

(b) isoprene: NOS, Sfc, 2006 (pptv)

(c) α-pinene: MAE, Sfc, 2006 (pptv)

(d) isoprene: MAE, Sfc, 2006 (pptv)

Fig. 2. Annual mean concentrations of *α*-pinene and isoprene at surface layer: **(a)** *α*-pinene without oceanic emission; **(b)** isoprene without oceanic emission; **(c)** *α*-pinene with MAE oceanic emission; **(d)** isoprene with MAE oceanic emission. MAE: "top-down" MAE prefactor emissions.

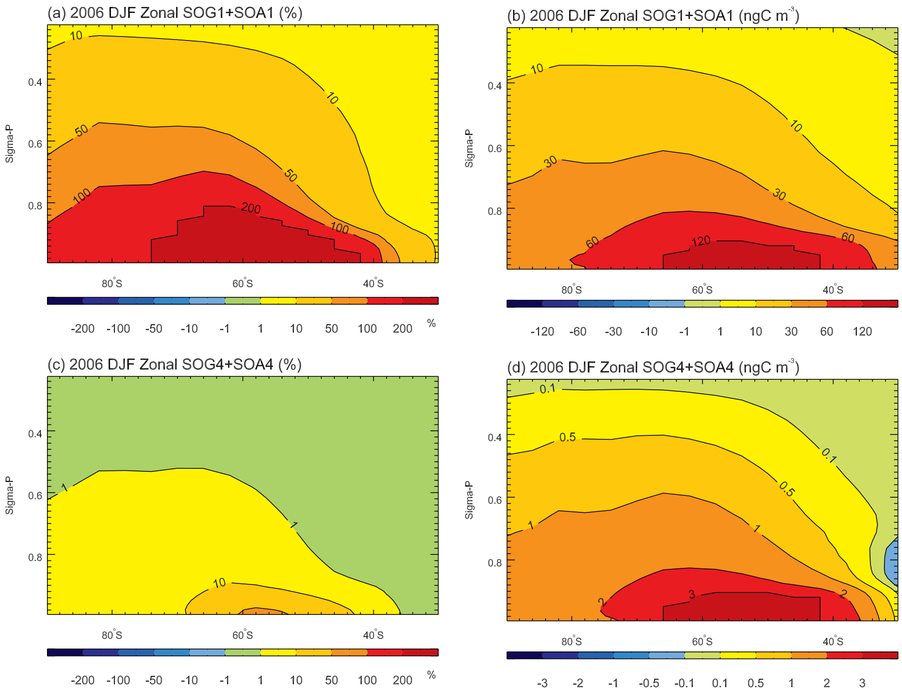


Fig. 3. Zonally-averaged latitudinal and vertical distributions of relative (**a** and **c**) and absolute (**b** and **d**) differences in SOG1+SOA1 (a and b) and SOG4+SOA4 (c and d) between the MAE case (with oceanic α-pinene and isoprene emissions) and the NOS case (without oceanic α-pinene and isoprene emissions) during the summer season (DJF) in the southern hemisphere. The y-axis sigma-pressure is defined as the ratio of pressure to surface pressure.

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