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**Oceanic isoprene and
marine OC aerosol**

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Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol

S. R. Arnold¹, D. V. Spracklen¹, J. Williams², N. Yassaa², J. Sciare³, B. Bonsang³, V. Gros³, I. Peeken⁴, A. C. Lewis⁵, S. Alvain³, and C. Moulin³

¹Institute for Climate and Atmospheric Science, School of Earth and Environment, University of Leeds, Leeds, UK

²Max Planck Institute for Chemistry, Mainz, Germany

³IPSL/LSCE, CEA Saclay, Gif-sur-Yvette, France

⁴Ifm GEOMAR, Kiel, Germany

⁵Department of Chemistry, University of York, York, UK

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Correspondence to: S. R. Arnold (s.arnold@see.leeds.ac.uk)

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Abstract

We have combined the first satellite maps of the global distribution of phytoplankton functional type and new measurements of phytoplankton-specific isoprene productivities, with available remote marine isoprene observations and a global model, to evaluate our understanding of the marine isoprene source and its impacts on organic aerosol abundances. Using satellite products to scale up data on phytoplankton-specific isoprene productivity to the global oceans, we infer a mean “bottom-up” oceanic isoprene emission of 0.31 ± 0.08 (1σ) Tg/yr. By minimising the mean bias between the model and isoprene observations in the marine atmosphere remote from the continents, we produce a “top-down” oceanic isoprene source estimate of 1.9 Tg/yr. We suggest our reliance on limited atmospheric isoprene data, and limited knowledge of isoprene productivity across the broad range of phytoplankton communities in the oceans as contributors to this difference between the two estimates. Inclusion of secondary organic aerosol (SOA) production from oceanic isoprene in the model with a 2% yield produces small contributions (0.01–1.6%) to observed organic carbon (OC) aerosol mass at three remote marine sites in the Northern and Southern Hemispheres. In addition, we find the seasonal cycle of the isoprene SOA source is out of phase with the observed cycle in OC in the remote Southern Ocean. Based on these findings we suggest an insignificant role for isoprene in modulating remote marine aerosol abundances, giving further support to a recently postulated primary OC source in the remote marine atmosphere.

1 Introduction

The globally extensive coverage of marine stratiform clouds means that they exert a significant influence on global climate. The physical characteristics of these clouds are significantly affected by oceanic sources of aerosol particles, which exert strong control on cloud condensation nuclei (CCN) concentrations in the relatively clean marine

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environment (O'Dowd et al., 1999). Knowledge of fundamental processes controlling aerosol abundances in the remote marine atmosphere is therefore critical to our ability to understand and predict the global climate. Sources of marine aerosol include primary emission of sea-salt particles by ocean white-cap generation and wave-breaking (Martensson et al., 2003), and dimethylsulfide from oceanic phytoplankton, which can be emitted into the marine atmosphere where it oxidises to produce sulphate aerosol (Andreae and Raemdonck, 1983; Grenfell et al., 1999). More recently, significant abundances of organic carbon (OC) aerosol have been observed in marine environments (Novakov et al., 1997; Putaud et al., 2000; Cavalli et al., 2004; Yoon et al., 2007; Pio et al., 2007), which are found to increase during periods of enhanced oceanic biological activity (O'Dowd et al., 2004). The mechanism and magnitude of the marine OC source are highly uncertain. Two recent studies have produced very different estimates of 8 Tg C/yr (Spracklen et al., 2008) and 75 Tg C/yr (Roelofs, 2008). Primary oceanic emission of OC particles driven by bubble-bursting processes ejecting particles from an organic film on the ocean surface (O'Dowd et al., 2004; Nillson et al., 2007), and secondary production of OC from oxidation of ocean-emitted gas-phase organic precursors (O'Dowd and de Leeuw, 2007) have both been postulated as sources of marine OC.

Phytoplankton in the oceans are known to produce a large suite of volatile organic compounds, including isoprene (2-methyl-1,3-butadiene, C₅H₈) (Moore et al., 1994; Shaw et al., 2003). Isoprene is a highly reactive di-alkene, and is rapidly oxidised in the atmosphere, leading to the formation of secondary organic carbon aerosol (Claeys et al., 2004; Liao et al., 2007). Production of secondary organic aerosol (SOA) from oceanic emission of isoprene from phytoplankton, and its impact on CCN concentrations, has been postulated as a mechanism to explain an observed reduction in cloud droplet effective radius and increase in cloud droplet number over a large phytoplankton bloom in the remote Southern Ocean (SO) during Austral Summer (Meskhidze and Nenes, 2006). Despite a significant downward revision of their initial estimate of isoprene emission derived during the study (Wingenter, 2007), the authors maintain

that a role for isoprene in the production of CCN cannot be ruled out, due to highly variable environmental conditions and variability in distributions of phytoplankton functional types (PFTs) encountered over the oceans (Meskhidze and Nenes, 2007).

Here, we attempt to quantify the contribution of isoprene to remote marine OC abundances based on current knowledge of biological and atmospheric processes, and available field and laboratory observations. We use new satellite observations of phytoplankton functional type (PFT) in the global oceans coupled with laboratory culture measurements of phytoplankton isoprene productivity to scale up a global isoprene emission estimate. A 3-D global chemical transport model is then used in conjunction with available atmospheric isoprene observations from the remote marine atmosphere to evaluate this global source. We identify key uncertainties and deficiencies in our understanding of the production, emission and fate of oceanic isoprene on the global scale.

2 Emission of isoprene from the oceans

Isoprene is produced by both phytoplankton (Broadgate et al., 1997; Ratte et al., 1998; Shaw et al., 2003) and seaweed (Broadgate et al., 2004) in the marine environment. A total global oceanic emission of 0.1–1.2 Tg C/yr has been estimated from in-situ observations (Bonsang et al., 1992; Milne et al., 1995; Broadgate et al., 1997) and satellite observations of ocean biological productivity (Palmer and Shaw, 2005), which is small compared with an estimated global terrestrial isoprene source of ~400–750 Tg C/yr (Muller et al., 2008; Guenther et al., 2006). Nevertheless, the high reactivity of isoprene means that an ocean source has the potential to perturb photochemistry in the remote marine atmosphere where reactive VOC loadings are small due to the distance from continental sources (e.g. Lewis et al., 2001).

A correlation between seawater isoprene concentration and chlorophyll-*a* concentration, [Chl-*a*], has been observed (Bonsang et al., 1992; Broadgate et al., 1997; Shaw et al., 2003), suggesting a relationship between isoprene production and phyto-

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plankton biological activity. This relationship, combined with global satellite observations of oceanic [Chl-*a*] has been used to derive a global oceanic isoprene emission of 0.11 Tg C/yr (Palmer and Shaw, 2005). This estimate assumed an invariant relationship between isoprene production and [Chl-*a*] observed across a range of three different PFTs in laboratory experiments (Shaw et al., 2003). More recent experiments suggest a variable relationship between isoprene production and [Chl-*a*] for different PFTs and individual species within PFTs (Bonsang et al., 2008¹). Table 1 shows rates of isoprene production in seawater for different PFTs from laboratory experiments, (for details see Bonsang et al., 2008¹). Phytoplankton cultures in their exponential growth phase were kept at a controlled temperature with a programmed light cycle of PAR (photosynthetic active radiation, 400–700 nm) simulating a diurnal cycle. The temperature and the PAR maximum intensity (30 or 100 $\mu\text{E m}^{-2} \text{s}^{-1}$) were chosen according to the natural habitat of the different cultures, particularly for diatoms characteristic of the Southern Ocean. Isoprene measurements were carried out by two different techniques: automated FID gas chromatography (Chromatotrapp GC/Chromatotec, Saint Antoine, France), with cryogenic trapping on Carbotrap B, Carbotrap C, Carbosieve S 111, and separation on PLOT, Al₂O₃/KCl capillary column, or collection on cartridges (Carbograph I/ Carbograph II; Markes International, Pontyclun, UK) and subsequent GC/MS analysis, (GC6890A, Agilent Technologies, CA, USA). Emission rates were determined from the composition change of synthetic air continuously flushed through the culture at a constant flow rate of 100 ml min⁻¹. Taking into account the measurement uncertainties and the isoprene detection limit of 0.5 pptv, emission rates are estimated with 10–15% uncertainty and with a detection limit of $\sim 0.2 \mu\text{mol g}[\text{Chl-}a]^{-1} \text{day}^{-1}$. The rate of seawater isoprene production is related to the chlorophyll-*a* concentration present in the sample. For each PFT, mean, standard deviation and maximum/minimum productivities were obtained for a number of individual species from a series of experiments. Production rates for skeletonema, a diatom species and *Emiliana huxley*, a haptophyte

¹Bonsang, B., Gros, V., Yassaa, N., Peeken, I., Bluhm, K., Zoellner, E., Sarda-Estevé, R., and Williams, J.: Isoprene emission from phytoplankton monocultures, in preparation, 2008.

agree well (+30% and +50%, respectively) with previous measurements by Shaw et al. (2003). For cyanobacteria, production rates are a factor ~ 6 (7.8 compared with $1.4 \mu\text{mol isoprene g[Chl-}a\text{]}^{-1} \text{ day}^{-1}$) larger than those observed by Shaw et al. (2003).

The distribution of different PFTs across the global oceans is highly variable spatially and temporally. This provides an additional challenge to quantifying marine isoprene fluxes, since the seawater isoprene production rate is dependent on the phytoplankton community composition in a given region, in addition to light and nutrient availability which determine phytoplankton biomass and the chlorophyll-*a* content per cell. Recent advances in satellite retrieval algorithms have allowed the spatial distribution of four different PFTs in the global oceans to be obtained from space for the first time. The method relies on the detection of spectral signatures from water-leaving radiances in the visible wavelengths, previously determined using the SeaWiFS (Sea Wide Field-of-view Sensor) satellite instrument and in-situ measurements from ship cruises (Dandonneau et al., 2004). The PHYSAT model (Alvain et al., 2005), uses this spectral information from SeaWiFS to produce global distributions of the dominant PFTs from four major phytoplankton groups (haptophytes, prochlorococcus, cyanobacteria and diatoms).

We produce global sea-air isoprene fluxes accounting for the variation in isoprene productivity across different PFTs, by combining remotely-sensed oceanic chlorophyll-*a* concentrations and PFT distributions from PHYSAT, with the laboratory isoprene productivity measurements shown in Table 1. Global monthly-mean seawater [Chl-*a*] are obtained from the SeaWiFS instrument. We assume that isoprene is in steady state and well mixed through the oceanic mixed layer depth (MLD), and that retrieved [Chl-*a*] values are representative of chlorophyll-*a* abundances over the MLD. Values of MLD are taken from a climatology based on measurements of ocean density and temperature (de Boyer et al., 2004). We use the assumptions of Palmer and Shaw (2005), who showed that timescales for isoprene loss in the water column by deep-water mixing and aqueous oxidation are long compared with loss by transfer across the sea surface. We therefore calculate our isoprene fluxes assuming that isoprene productivity

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in the ocean is balanced by sea-air exchange. The short atmospheric lifetime of isoprene means the exchange can be considered unidirectional. In the limit that oceanic losses of isoprene over the MLD are negligible, our emissions can be considered upper estimates.

5 To account for the observed range of isoprene productivities for individual phytoplankton species, and the different species sampled within an individual PFT, probability distribution functions (PDFs) of isoprene production rate are constructed for each of the four PFTs mapped by PHYSAT. For each PFT, a mean productivity value and mean fractional standard deviation are calculated, and maximum and minimum values
10 are taken, from the sampled species belonging to the group (Table 1). For diatoms, a distinction is also made between species characteristic of the Southern Ocean and the remainder of the oceans (for details see Bonsang et al., 2008¹). The Southern Ocean values are applied south of 50° S, the approximate latitude of the oceanic polar front. Productivity PDFs for each PFT are constructed as Gaussian functions using
15 the mean and standard deviation values, and the distribution tails are truncated at the maximum and minimum observed values for the group. This restricts the range of productivity values to those observed, and prevents the occurrence of negative values in the tails of the distributions. Alvain et al. (2005) showed that over some regions of the global oceans, the PHYSAT method is unable to detect the dominant PFT. This is
20 due to large aerosol optical thickness values over e.g. the Indian Ocean and equatorial Atlantic Ocean, or the presence of phytoplankton assemblages with optical properties which have not been sampled. For these regions, we construct a PDF of isoprene productivity using the mean value and mean fractional standard deviation, and overall maximum and minimum, from all phytoplankton groups in Table 1. This allows the full
25 range of possible isoprene productivities to be accounted for, but results in a weaker constraint on isoprene emission from these regions.

A Latin-Hypercube sampling method (McKay et al., 1979) was used to produce a Monte-Carlo ensemble of global isoprene emission scenarios from the PFT productivity PDFs, global fields of SeaWiFS chlorophyll-*a* and PHYSAT distributions. Each

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of the PDFs was split into 500 bins of equal probability, and bins were randomly selected from each PDF to be applied to the chlorophyll-*a* and PHYSAT distribution fields. This produced an ensemble of 500 global isoprene emission fields, weighted by the PDFs of the isoprene production rates for each PFT. The resulting PDF of global total isoprene emission is shown in Fig. 1. The ensemble mean total annual emission is 0.31 Tg/yr, with 5th/95th percentile values of 0.18 and 0.45 Tg/yr. This range of values is close to some previous estimates inferred from in-situ isoprene observations (0.19 Tg/yr (Broadgate et al., 1997); 0.38 Tg/yr (Milne et al., 1995)), but significantly less than others (1.2 Tg/yr (Bonsang et al., 1992)). A previous global estimate using remotely-sensed chlorophyll-*a*, but applying a single chlorophyll-isoprene productivity relationship, inferred an emission of 0.11 Tg/yr (Palmer and Shaw, 2005), which is at the lower limit of our estimated range. The annual mean isoprene emission flux from the ensemble mean using chlorophyll-*a* and PHYSAT distributions from the year 2000 is 0.27×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$, with a range of 1.3×10^5 to 1.6×10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$. Despite being 3 orders of magnitude less than the terrestrial isoprene source, the inferred ocean source substantially enhances model isoprene concentrations over large areas of the remote oceans by up to 4 orders of magnitude where terrestrial sources have no influence (Fig. 2).

3 Evaluation of marine isoprene emissions

We include our calculated isoprene emissions in the GEOS-Chem global chemical transport model (v7.04) (Bey et al., 2001; Park et al., 2003), and evaluate them using observations of isoprene in the remote marine atmosphere. Few isoprene observations have been made in regions remote from the continents, with most marine observations being made at continental coastal sites. Figure 2d demonstrates that the expected contribution from the oceanic source to surface isoprene concentrations is swamped by terrestrial emissions at coastal sites. Without careful filtering to mask continental influence, such observations may be unsuitable for the evaluation of the relatively small

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ocean source under discussion here. We include in this analysis isoprene measurements made in the marine BL at least 1-degree in longitude and latitude from any land. Table 2 details the available isoprene observations for model evaluation fitting these criteria. A small number of aircraft observations are available from the ITOP experiment over the mid North Atlantic ocean (Lewis et al., 2007), where the aircraft sampled near-surface marine air north-west and south-east of the Azores in July 2004. Limited periods of more frequent measurements are available from ship cruises in the marine surface atmosphere of the western North Pacific during May 2001 (Matsunaga et al., 2002) and the remote Southern Indian Ocean during December 1997 (Yokouchi et al., 1999). Isoprene observations were also made during the ARCICE cruise at 80° N in the Arctic Ocean during August 1999 (Hopkins et al., 2002). Individual isoprene measurements are not quoted for this study, and we compare with a mean concentration value given for this latitude over the cruise period.

Figure 3 compares these observations with model monthly-mean surface atmosphere isoprene concentrations from simulations including and neglecting our 0.31 Tg/yr oceanic isoprene source. Model output is taken from the model grid-box corresponding to the location and month of each observation point. Without an oceanic isoprene source, the model severely underpredicts observed isoprene by up to 4 orders of magnitude (mean bias (MB) -27 pptv; normalised mean bias (NMB) -99.6%). Table 2 shows model bias values for each observation set. The short lifetime of isoprene means that transport from terrestrial sources cannot account for its abundance in the remote marine BL. This highlights the role of marine emissions in controlling remote marine background isoprene concentrations. Including the 0.31 Tg/yr oceanic isoprene source reduces the model underprediction (MB -24 pptv; NMB -91%), however the observations remain underestimated by the model. This underprediction is greatest for the cruise observations in the North West Pacific. Matsunaga et al. (2002) demonstrated that air masses sampled on this cruise were likely to be influenced by outflow from Asia, and not representative of the remote marine atmosphere. Omitting these observations from the analysis improves the model performance (MB -17 pptv;

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NMB –85%). We globally scale our 0.31 Tg/yr bottom-up source to minimise bias between the observations (excluding those of Matsunaga et al., 2002) and the model. We find the best match (MB –2.1 pptv; NMB –11%) with a global scaling factor of 6. This produces an effective “top-down” emission estimate of 1.9 Tg/yr.

Several factors may contribute to the inconsistency between observed marine BL isoprene concentrations and our bottom-up isoprene emission estimate. A bias in satellite-retrieved Chl-*a* concentrations translates directly to a bias in the derived isoprene flux. Moreover, the assumption that remotely-sensed Chl-*a* concentrations are representative over the ocean MLD may be incorrect and lead to errors in the emission calculation. Inconsistencies between the MLD climatology used in the emission calculation and the true ocean MLD in the regions of the observations would also produce errors in the calculated fluxes. The global improvement in model-observation bias produced by application of a single scaling factor of ~6, would translate to a significant global-scale bias in satellite chlorophyll-*a* concentrations or MLD climatology values. Based on past evaluations of these products (de Boyer et al., 2004; Marrari et al., 2006), a systematic bias of such magnitude seems unlikely. The assumption that isoprene is well-mixed through the MLD is an approximation. Observations of isoprene over the oceanic vertical column show a vertical gradient with an isoprene maximum slightly shallower than the chlorophyll-*a* maximum at 40–60 m depth (Bonsang et al., 1992; Milne et al., 1995; Moore and Wang, 2006). We assume that our isoprene emission flux is chiefly determined by an equilibrium between isoprene production by phytoplankton in the near-surface column and loss to the atmosphere, with losses and exchanges in the water column being of second order importance (Shaw et al., 2003; Palmer and Shaw, 2005). The mixing of isoprene and phytoplankton from larger depths may increase isoprene in the near-surface ocean, however the isoprene/chlorophyll-*a* ratio would not be expected to change significantly, and this is unlikely to account for a large bias in our emission estimates.

For the phytoplankton species sampled in the laboratory experiments, we assume that near-maximum isoprene production rates were observed, since measurements

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were taken during the exponential growth phase, when previous studies have observed maximum production compared with smaller production rates during the population senescence phase (Shaw et al., 2003). Given the large variability in isoprene productivities within a given PFT (Table 1), it is possible that as yet unsampled species may produce larger amounts of isoprene than is accounted for by our emission calculations. Isoprene may be more readily produced by species communities in the real oceans than by the selection of single-species cultures sampled in the controlled experiments. The underlying assumption in our method is that the combination of emission rates from several phytoplankton monocultures is representative of the phytoplankton community emission, which is not necessarily valid.

In-situ measurements of ocean isoprene fluxes have been taken in a few locations. Matsunaga et al. (2002) observed fluxes between 0.2×10^8 and 2.1×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ during their cruise in the North Pacific in September 2001. Our mean flux values for this location and month are 0.19×10^8 and 1.1×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ for the 0.31 and 1.9 Tg/yr sources, respectively, with overall minimum and maximum values of 0.10×10^8 and 1.80×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$, giving good agreement with the observed fluxes. A mean flux value of 1.1×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ was observed during May 1987 in a similar region (Bongsang et al., 1992). The PHYSAT model indicates that haptophytes are strongly dominant at this location and time of year, providing a relatively narrow constraint on the isoprene source in this region. Using a single invariant chlorophyll-dependent isoprene productivity across the globe, Palmer and Shaw (2005) found that they were unable to reproduce observed fluxes in this region, with an underestimate of 1–2 orders of magnitude. Isoprene fluxes observed in the Straits of Florida during September 1993 were between 0.06×10^8 and 0.7×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$. Our flux estimates for this region and month range from 0.04×10^8 to 1.7×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ for the 0.31 and 1.9 Tg/yr sources, with mean values of 0.07×10^8 and 0.42×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$, respectively, again demonstrating good agreement with the observations. In the North Atlantic ocean, there is evidence that our estimated fluxes (0.25 – 1.5 molecules $\text{cm}^{-2} \text{s}^{-1}$)

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for the smaller 0.31 Tg/yr source) are large compared with observed fluxes of 0.08×10^8 to 0.6×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ during May 1997 (Baker et al., 2000).

4 Impacts on marine organic carbon aerosol

The role of isoprene as a precursor for organic aerosol formation has led to the suggestion that oceanic isoprene emissions may exert control on marine OC aerosol and CCN abundances over the remote Southern Ocean (Meskhidze and Nenes, 2006). We have estimated the contribution of both our best-estimate bottom-up (0.31 Tg/yr) and top-down (1.9 Tg/yr) emissions to global and regional OC concentrations, by including a 2% yield of secondary organic aerosol (SOA) from isoprene (Henze and Seinfeld, 2006) in the GEOS-Chem model simulations. Formation of SOA is treated immediately on emission of the marine isoprene. Therefore estimated contributions to OC abundances are an upper limit for the given SOA yield and isoprene emission. On a global scale, with the 2% yield, our bottom-up and top-down emissions contribute 0.006 Tg/yr and 0.04 Tg/yr of organic carbon aerosol respectively. Based on in-situ observations of OC in the remote marine BL, Spracklen et al. (2008) recently inferred a chlorophyll-*a* dependent global marine OC source of ~ 8 Tg/yr. Our two isoprene source estimates therefore, respectively, account for 0.08% and 0.5% of the proposed marine OC source globally. An increase in the isoprene SOA yield would translate to an increased significance for oceanic isoprene in marine OC. Yields of SOA from in-cloud processing of isoprene oxidation products of up to 42% have recently been observed in highly polluted environments ($[\text{C}_5\text{H}_8]/[\text{NO}_x] \sim 0.05$) (Ervens et al., 2008). An upper limit of 0.78 Tg/yr of SOA from the top-down 1.9 Tg/yr isoprene source is obtained by applying the maximum 42% SOA yield globally. This equates to a maximum $\sim 10\%$ of the estimated 8 Tg/yr source of marine OC. However, the low NO_x concentrations characteristic of the remote marine atmosphere (on the order 10 pptv or less) will produce substantially smaller SOA yields through this process. Ervens et al. (2008) found yields of between 2 and 3% at $[\text{C}_5\text{H}_8]/[\text{NO}_x]$ concentration ratios similar to those found

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under typical marine conditions with our 1.9 Tg/yr isoprene source (~30 pptv isoprene, ~10 pptv NO_x). These are close to the 3% yields observed during studies of isoprene SOA production under gas-phase oxidation in low-NO_x conditions (Kroll et al., 2006).

5 Observations of monthly-mean marine BL OC concentrations have recently become available at Amsterdam Island (37°31' S, 77°19' E) in the remote Southern Indian Ocean (Sciare et al., 2008²). These observations have been used in conjunction with equivalent datasets from the Azores (38°41' N, 27°21' W) (Pio et al., 2007) and Mace Head, Ireland (53°20' N, 9°54' W) (Yoon et al., 2007) to infer the estimated 8 Tg/yr source of OC from the global oceans (Spracklen et al., 2008). Figure 4 compares the annual cycle of OC observed at these sites with GEOS-CHEM modelled OC from simulations without an oceanic isoprene OC source, and with 2% SOA production from the bottom-up (0.31 Tg/yr) and top-down (1.9 Tg/yr) emission fields. At Amsterdam Island, maximum contributions of 0.2% and 1.3% from oceanic isoprene SOA to OC mass are obtained for the smaller and larger isoprene sources respectively using the model 2% isoprene SOA yield. This suggests an insignificant role for isoprene in driving marine OC abundances in this region of the Southern Ocean. We find the maximum OC contribution from isoprene is in spring (September), with the smallest contribution in summer (January–February), out of phase with the observed annual cycle of OC, which shows a strong peak in summer and minimum in winter. Our calculation assumes isoprene emission is directly proportional to both ocean chlorophyll-*a* content and the ocean MLD. The seasonality in the ocean isoprene source is therefore driven by the annual cycles in both of these quantities. MLD values reach their minimum during the summer months in this region (de Boyer et al., 2004), which gives rise to peak isoprene emission in spring and minimum emission in summer, despite a summertime peak in chlorophyll-*a*. Since OC production from isoprene is modelled as a 2% conversion of isoprene carbon mass at emission, our seasonality in isoprene con-

²Sciare, J., Sarda-Estave, R., Favez, O., Oikonomou, K., and Cachier, H.: Seasonal variations of carbonaceous aerosols in the Austral Ocean: Evidence of a marine biogenic origin, *J. Geophys. Res.-Atmos.*, to be submitted, 2008.

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tribution to OC is driven by seasonality in the emission flux. This is a simplification, in that we neglect gas-phase oxidation of atmospheric isoprene to produce condensable organic aerosol products. Taking our assumptions and simplifications to be valid, and assuming the magnitudes and seasonal pattern of the MLD climatology are reasonably realistic, this leads to the conclusion that a dominant role for isoprene in producing OC in the remote Southern Ocean would produce a seasonal variation in OC concentrations different from that observed. However, our limited understanding of how isoprene over the MLD column contributes to ocean surface emission, and our simplification of oceanic isoprene OC production in the model means that it is not possible to verify this hypothesis. Decoupling the seasonality in our isoprene OC production from observed OC, we produce a maximum possible isoprene contribution to marine OC of 1.3% at Amsterdam Island, from the maximum modelled isoprene production of OC (October) and the minimum observed OC (June).

The maximum isoprene SOA contribution to OC at the Azores occurs in March, and amounts to 0.14% and 0.84% of the observed OC from simulations using the 0.31 Tg/yr and 1.9 Tg/yr emissions, respectively. This is coincident with when the minimum OC concentration is observed. The maximum OC is observed in July, where the isoprene SOA contribution is close to its minimum (0.01–0.07%). At Mace Head, simulations with the 0.31 Tg/yr and 1.9 Tg/yr emissions produce a maximum isoprene SOA contribution to observed OC of 0.24% and 1.4%, respectively. This occurs in March, close to the maximum in chlorophyll-*a* concentration in this region (April). Minimum contributions (0.01–0.04%) occur in November close to the minimum in chlorophyll-*a* (December). Decoupling the modelled isoprene OC and observed OC seasonal cycles produces maximum isoprene contributions to OC of 0.91% and 6.2% at the Azores and Mace Head, respectively.

At all three sites, the model severely underpredicts observed OC concentrations. The 8 Tg/yr oceanic OC source proportional to ocean chlorophyll-*a* concentration derived by Spracklen et al. (2008) was shown to produce a significant improvement in the model performance. Those emissions did not include a MLD dependence, and

reproduced well the observed seasonal OC cycles. Our modelled contributions to OC from SOA production at these sites are at most $\sim 6\%$, assuming a 2% SOA yield from isoprene.

5 Conclusions and recommendations

5 We have combined laboratory measurements of phytoplankton isoprene productivity, satellite datasets on ocean biology, available field observations and a global atmospheric chemistry model to estimate and evaluate the global oceanic isoprene source. We have introduced a refinement to previous attempts to use satellite chlorophyll-*a* data to scale-up estimates of phytoplankton trace-gas emissions to the global oceans (Simo and Dachs, 2002; Palmer and Shaw, 2005), by including for the first time information on the distribution of phytoplankton functional type in the global oceans. This has reduced differences between observed oceanic isoprene fluxes and emissions calculated using this method assuming a single isoprene productivity-chlorophyll-*a* relationship. However, large uncertainties remain in our global emission estimates. Using a Monte-Carlo ensemble method to project uncertainty in isoprene emission rates for specific phytoplankton species and classes onto the global satellite maps, we produce a near-Gaussian distribution of global emissions with a mean value of 0.31 Tg/yr and standard deviation 0.08 Tg/yr. This “bottom-up” estimate appears to be inconsistent with a limited collection of isoprene concentration measurements in the marine BL at locations remote from continental influence. A factor ~ 6 increase in the mean emission is required to minimise the model-observation mean bias, producing a “top-down” emission estimate of 1.9 Tg/yr. This offset is not easy to explain, and we suggest that the presence of as yet unsampled strong isoprene emitters in phytoplankton communities across the oceans may be at least partly responsible. Additionally, the lack of atmospheric isoprene observations in regions remote from continental influence means that our top-down estimate is strongly biased by the limited datasets used here, which may or may not be representative of remote marine isoprene abundances on a larger

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scale. In regions of the remote marine atmosphere where the continental contribution to isoprene is negligible (<0.1 pptv), phytoplankton appear to be capable of maintaining isoprene abundances of 10s pptv over large areas. Over biologically active regions of the global oceans, such concentrations may lead to abundances of oxidation products (e.g. HCHO) capable of acting as a significant photochemical radical source.

The uncertainties in the global marine isoprene source presented here can only be reduced by both further testing of different phytoplankton species for isoprene productivity and by increasing the available observations of isoprene abundances over biologically active and inactive oceans in regions remote from continental influence. It may be possible to design strategies by which satellite products such as PHYSAT could be used to target observations to a particular region where the dominance of certain PFTs are predicted. In addition, a better understanding of how combinations of individual phytoplankton isoprene productivities compare with true community isoprene productivities can be gained from direct measurement of isoprene production from phytoplankton communities from the oceans.

Based on current understanding of isoprene SOA yields, isoprene appears to be an insignificant source of OC in the remote marine atmosphere. With a 2% SOA yield, our larger “top-down” emission estimate produces 0.04 Tg/yr OC aerosol, which represents only 0.5% of a recently estimated 8 Tg/yr global source of oceanic OC aerosol (Spracklen et al., 2008). At three remote marine sites, SOA production from phytoplankton isoprene contributes a maximum of 1.5% to observed OC abundances. Decoupling the seasonality in isoprene OC production from the observed seasonal cycle in OC to remove our reliance on assumptions regarding factors driving the seasonality of isoprene OC production, would produce a maximum contribution of $\sim 6\%$. An increase in this contribution to a significant fraction of marine OC would require either a large increase in the isoprene SOA yield, or a strong enhancement to the oceanic isoprene flux, to produce regionally-enhanced marine BL isoprene abundances significantly larger than those observed to date. Assuming a 2% OC mass yield from isoprene, a global marine isoprene source of ~ 400 Tg/yr would be required to account

for the recently-estimated 8 Tg/yr global source of marine OC (Spracklen et al., 2008). Such a large source would produce atmospheric isoprene concentrations over the remote oceans orders of magnitude larger than observed. These findings support a non-dominant role for isoprene in driving OC abundances in the remote Southern Ocean, lending support to the postulation of a primary marine OC source (O'Dowd et al., 2004; Spracklen et al., 2008).

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Table 1. Isoprene production rates measured in controlled single-species culture experiments for the four phytoplankton classes considered by the PHYSAT model. Data from Bonsang et al. (2008)¹. Data presented as mean \pm 1 σ (min/max).

Class	Isoprene production rate ($\mu\text{mol isoprene g}[\text{Chl-}a]^{-1} \text{ day}^{-1}$)
Haptophytes	1.99 \pm 1.00 (1.24/2.73)
Prochlorococcus	9.66 \pm 5.78 (2.40/22.1)
Cyanobacteria	7.83 \pm 3.02 (2.40/22.1)
Diatoms (S Ocean)	1.21 \pm 0.57 (0.33/1.99)
Diatoms (elsewhere)	2.48 \pm 1.75 (0.00/10.1)
Unidentified	3.13 \pm 1.57 (0.00/22.1)

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Table 2. Observations of boundary layer isoprene concentrations taken in the non-coastal marine boundary layer. Mean bias and normalised mean bias between model and observations are shown from model simulations without an oceanic isoprene source, and with a 0.31 Tg/yr and a 1.9 Tg/yr isoprene source.

	Location	Month	Reference	Isoprene /pptv ^a	Mean Bias ^b /pptv		
					No source	0.31 Tg/yr	1.9 Tg/yr
ITOP	North Atlantic	Jul	Lewis et al. (2007)	–(3.7/2.7)	–3 (–100%)	–3 (–84%)	–0.14 (–5%)
Ship Cruise	40–110° E, S. Ocean	Dec	Yokouchi et al. (1999)	17 (60/1.4)	–22 (–100%)	–19 (–86%)	–3.6 (–16%)
ARCICE	80° N, Norwegian Sea	Aug	Hopkins et al. (2002)	2 (–/–)	–2.0 (–99%)	1.6 (78%)	20 (995%)
Ship Cruise	North West Pacific	May	Matsunaga et al. (2002)	46 (110/7.2)	–45 (–100%)	–45 (–98%)	–42 (–92%)

^a Isoprene concentrations shown as median (max/min).

^b Shown as model mean bias (normalised mean bias (%)).

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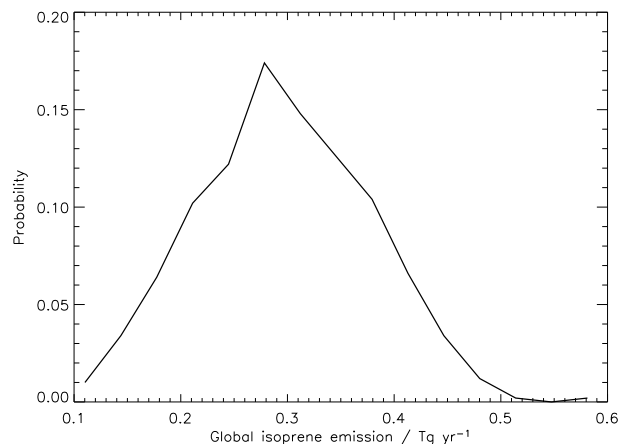


Fig. 1. Probability distribution function of global oceanic isoprene emission totals from a 500-member Monte-Carlo ensemble simulation. The simulation projects variability in seawater isoprene productivity for each phytoplankton class (Table 1) onto global satellite maps of chlorophyll-*a* and phytoplankton class. See text for details.

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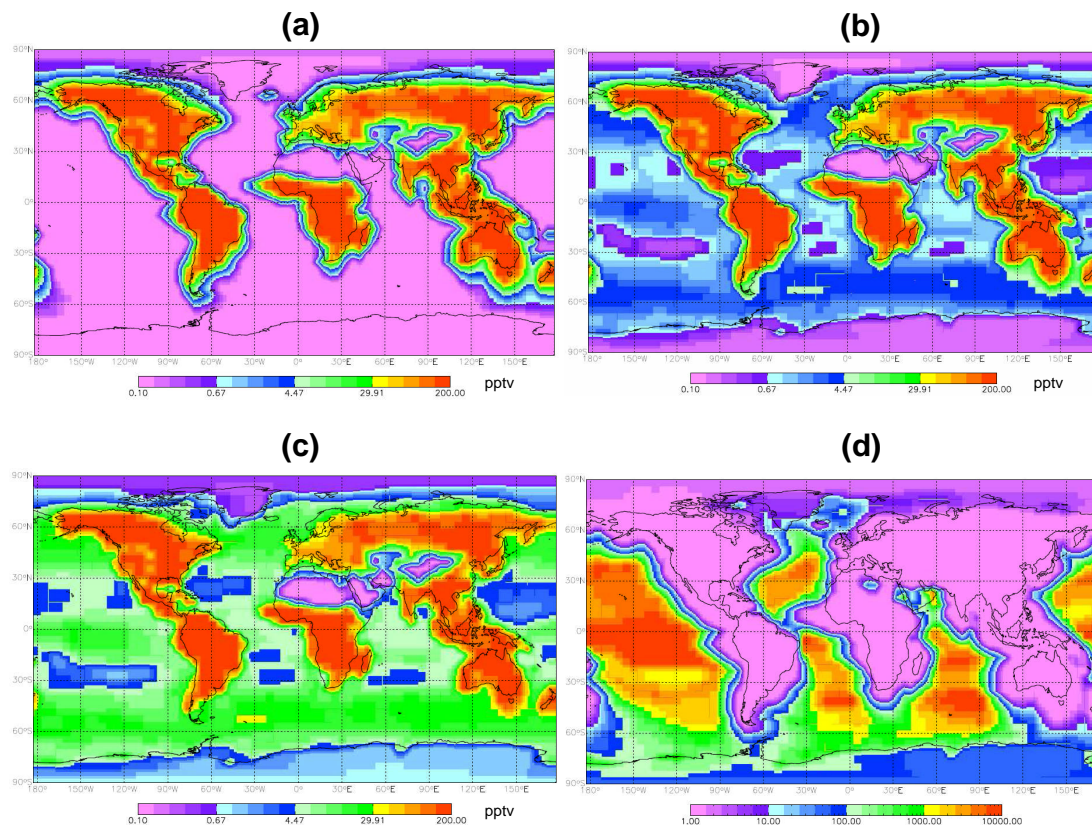


Fig. 2. (a–c) Annual mean surface atmospheric isoprene concentrations from the GEOS-CHEM model for year 2000 from simulations (a) without an oceanic isoprene source, (b) with the 0.31 Tg/yr “bottom-up” source estimate, and (c) with the 1.9 Tg/yr “top-down” source estimate. (d) Ratio of annual mean surface atmospheric isoprene concentrations from the 1.9 Tg/yr oceanic source to the no oceanic isoprene source simulations (panel c/a). Note colour scale is saturated at highest and lowest colour-bar values.

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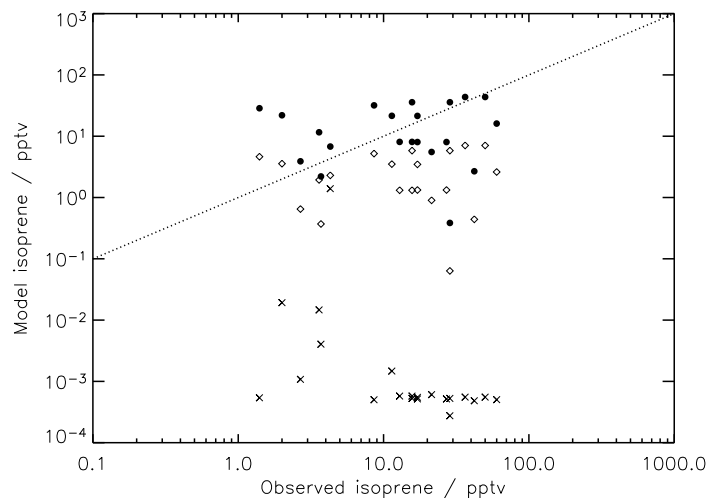


Fig. 3. Scatter plot of observed versus GEOS-CHEM simulated isoprene concentrations in the remote marine boundary layer at locations and times given in Table 2. Crosses (x): no oceanic isoprene emissions; diamonds (◊): “bottom-up” 0.31 Tg/yr emissions; filled circles: “top-down” 1.9 Tg/yr emissions.

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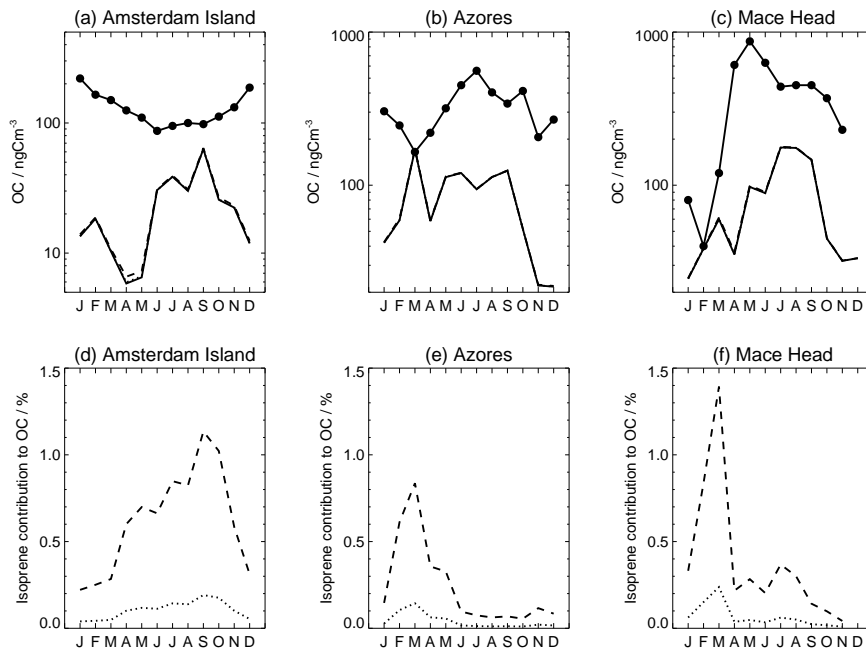


Fig. 4. Top panels: Observed (solid line, filled circles) and modelled OC aerosol concentrations at the three remote marine sites **(a)** Amsterdam Island (37°31' S, 77°19' E), **(b)** Azores (38°41' N, 27°21' W), **(c)** Mace Head (53°20' N, 9°54' W), using a 2% SOA yield from isoprene with no oceanic isoprene emission (solid line), 0.31 Tg/yr oceanic isoprene emission (dotted line) and 1.9 Tg/yr oceanic isoprene emission (dashed line). Bottom panels: Percentage contribution of model SOA from oceanic isoprene emissions to observed OC for 0.31 Tg/yr oceanic isoprene emission (dotted line) and 1.9 Tg/yr oceanic isoprene emission (dashed line) at **(d)** Amsterdam Island, **(e)** Azores, **(f)** Mace Head.

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