Quantifying global marine isoprene fluxes using MODIS chlorophyll observations

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[1] We report global distributions of marine isoprene flux, whose source is estimated by combining an empirical relationship for isoprene production rate with MODIS satellite chlorophyll observations from 2001. We use a steady-state water column model including losses to chemistry, bacteria, and air-sea exchange. Physical mixing is a negligible sink. Flux estimates range from $10^7 - 10^9$ molecules cm^{-2}s^{-1}, with considerable spatial and temporal variability, resulting in a global annual total of 0.1 Tg C/yr. Air-sea exchange is the dominant isoprene sink in the surface oceans, with bacteria the second largest, but much less important, sink. The reported fluxes represent a small loss of OH in the remote marine boundary layer (MBL) compared to other oxidants. Application of our approach to other reactive compounds may improve a priori flux estimates for coupled atmosphere-ocean biogeochemistry inverse model studies. **Citation:** Palmer, P. I., and S. L. Shaw (2005), Quantifying global marine isoprene fluxes using MODIS chlorophyll observations, Geophys. Res. Lett., 32, L09805, doi:10.1029/2005GL022592.

1. Introduction

[2] Isoprene (C_5H_8) is a reactive biogenic hydrocarbon that affects oxidant chemistry in the troposphere, organic aerosol formation, and climate. Terrestrial isoprene originates primarily from photosynthetic vegetation [*Guenther et al.*, 1995], with the tropics responsible for most of the global annual total (~500 Tg C/yr). The oceans also emit isoprene, with phytoplankton and seaweed the only known sources; all species tested have this capability [e.g., *Bonsang et al.*, 1992; *Ratte et al.*, 1998; *Shaw et al.*, 2003; *Broadgate et al.*, 2004]. Estimated global marine isoprene fluxes extrapolated from in situ measurements range from 0.2–1.2 Tg C/yr. These values are small compared to terrestrial fluxes, but the high reactivity of isoprene (~1–2 hour lifetime) means marine emissions have the potential to impact local remote MBL chemistry.

[3] Marine isoprene fluxes are highly variable in time and space because phytoplankton biomass is sensitive to parameters such as light and nutrient availability that are a function of ocean biology and dynamics. The paucity of in situ measurements, combined with a poor understanding of the processes controlling marine isoprene, has made reliable regional and global isoprene flux estimates, and thereby an assessment of their impact on chemistry and climate, difficult. However, recent laboratory culture work exhibited a simple and robust relationship between isoprene production rate and cellular chlorophyll content [*Shaw et al.*, 2003] that lends itself well to scaling and allows us to take advantage of remotely sensed data sets. We use this relationship to calculate high resolution, global monthly mean air-sea isoprene flux estimates with a steady state model of estimated production and loss terms. Global and zonal fluxes are presented, and their importance on regional remote MBL photochemistry is assessed.
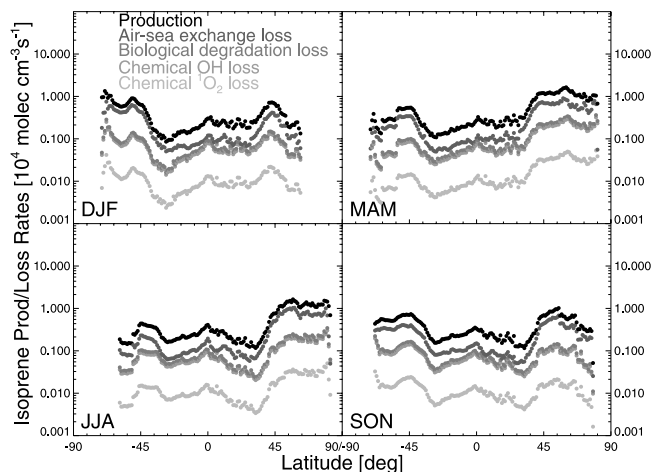
2. Water Column Production and Loss Rates

[4] Calculation of the air-sea isoprene flux requires solving the ocean mass balance. Recent depth profiles show no isoprene accumulation over several week periods [*Moore and Wang*, 2005], so we assume it is in steady state over a month:

$$P - C_W \left(\Sigma k_{CHEM,i} C_{Xi} - k_{BIOL} - k_{AS}/Z_{ML} \right) - L_{MIX} = 0,$$

where P is production, C_W is the seawater concentration, k variables are loss rate constants, and Z_{ML} is the ocean mixed layer (ML) depth. The second term is loss due to chemical degradation summed over all reactants X, the third is bacterial loss; and the fourth is loss due to air-sea exchange. L_{MIX} is the loss due to physical mixing down to the deep ocean. Figure 1 shows the 2001 seasonal zonal mean values of the individual terms.

[5] *Shaw et al.* [2003] tested several cyanobacteria, eukaryotes, and a coccolithophore, and found an invariant relationship of 1.8 ± 0.7 μmoles isoprene produced (g phytoplankton chlorophyll-a)$^{-1}$day^{-1}. This is likely due to the source of isoprene being either a product of enzymatic transformation, or non-enzymatic hydrolysis, of chlorophyll biosynthesis intermediates. P is estimated by multiplying this factor with global maps of remotely sensed chlorophyll concentrations from the moderate resolution imaging spectroradiometer [*Carder et al.*, 2004] (MODIS) instrument onboard the Terra satellite. The MODIS instrument was launched in December 1999 in a sun-synchronous orbit, achieving global coverage in 1–2 days. It has a local overpass time of 10:30 and a spatial resolution of 1 km. We use chlorophyll-a data retrieved using the semi-analytical algorithm of *Carder et al.* [2004] with a horizontal resolution of 36 km^2, which have uncertainties typically <40%, and quality flags of 0 or 1.

Figure 1. Zonal mean isoprene production and loss rates (10^4 molec cm^{-3} s^{-1}) as a function of latitude and season for 2001. Positive latitudes are in the Northern Hemisphere. See color version of this figure in the HTML.

Production rates are largest during springtime in each hemisphere (Figure 1).

[6] Chemical loss due to reaction with oxidative transients is the most important aqueous chemical sink for other light alkenes [*Riemer et al.*, 2000], and likely isoprene. Information on some relevant transients (O_3, O_2^-, H_2O_2) is not available; but losses to OH and $^1O_2$ can be estimated. These rates ($k_{OH} = 6 \times 10^{10}$ M^{-1}s^{-1}, http://www.iupac-kinetic.ch.cam.ac.uk; $k_{1O2} = 10^6$ M^{-1}s^{-1} [*Monroe*, 1981]) are scaled by the seawater concentrations of the relevant oxidant (OH = 10^{-17} M and $^1O_2 = 10^{-14}$ M) [*Cooper et al.*, 1989] and isoprene, C_W, leading to turnover times of 19 and 115 days respectively. Reactions of other alkenes with RO_2 have estimated half-lives of ~900 days [*Mill et al.*, 1978], so we neglect this reaction. Chemical losses are typically <10% of the production rate (Figure 1).

[7] It is not currently known if marine bacteria can oxidize isoprene. Lab experiments showed no loss to various species [*Shaw et al.*, 2003], although recent field measurements show indirect evidence of a biological sink [*Moore and Wang*, 2005]. Soil bacteria can consume isoprene [e.g., *Cleveland and Yavitt*, 1998], and it seems likely some marine species can as well. We run two cases, with and without a bacterial loss, the latter with rates similar to those for methyl bromide (CH_3Br) because these gases undergo similar ocean biogeochemistry, and there are self-consistent data sets available for CH_3Br consumption from many locations [e.g., *Yvon-Lewis et al.*, 2002; *Tokarczyk et al.*, 2003]. We use a single global average value of $k_{BIOL} = 0.06$ day^{-1}, resulting in a mean isoprene lifetime against bacterial consumption of 17 days. This is the second largest loss term but values are typically $\ll$ air-sea exchange (Figure 1). Neglecting this sink results in a 27% increase in the global annual isoprene flux, but no other significant changes to our conclusions.

[8] The air-sea flux F is parameterized by

$$F = k_{AS}(C_W - C_A H),$$

where k_{AS} is the gas exchange coefficient (m s^{-1}), C_A is the atmospheric isoprene concentration, and H is the dimen-

sionless Henry's law constant. The main atmospheric isoprene sink is oxidation by OH, leading to a lifetime of about an hour. Consequently, we assume C_A is zero in the remote MBL. We use the *Wanninkhof* [1992] formulation to determine k_{AS}

$$k_{AS} = 0.31 \cdot U^2 (S_C/660)^{-0.5},$$

where U is the monthly-mean surface wind speed (we use QuikSCAT satellite data [*Wanninkhof et al.*, 2004]) and S_C is the Schmidt number.

[9] We estimate S_C following *Moore and Groszko* [1999], using an isoprene molal volume of 103.6 cm^3 g mol^{-1} [*Reid et al.*, 1977]. We calculate $S_C = 3913.15 - 162.13$ T$_C$ + 2.67 T$_C^2$ − 0.012 T$_C^3$, where T$_C$ is sea surface temperature (°C) from MODIS [*Brown et al.*, 2002]. To estimate the isoprene lifetime against air-sea exchange we scale k_{AS} with monthly mean climatological Z_{ML} values [*de Boyer Montégut et al.*, 2004]. In reality the MODIS chlorophyll concentrations represent a vertically weighted average over the sensed optical depth and not the ML depth. We assume the chlorophyll is well mixed so the retrieved values are representative of the entire ML. Typical values for k_{AS}/Z_{ML} are 1×10^{-6} s^{-1}, leading to a lifetime of 7 days. Air-sea exchange is the dominant loss term at all latitudes (Figure 1).

[10] We estimate the net isoprene loss through the thermocline, L_{MIX}, by adapting the approach of *Yvon-Lewis et al.* [2002]. This loss rate is given by $(D_z/Z_{ML})(\Delta C/\Delta Z)$, where D_z is the thermocline diffusivity (m^2 d^{-1}) and $\Delta C/\Delta Z$ is the concentration gradient across the thermocline (moles m^{-3}m^{-1}). Note these authors used the gradient *below* the ML because they investigated a uniform depth profile in a well-mixed eddy. We assume their average D_z value of $1 \pm 0.4 \times 10^{-4}$ m^{2}s^{-1} [*Yvon-Lewis et al.*, 2002], and use the isoprene depth profile from *Milne et al.*
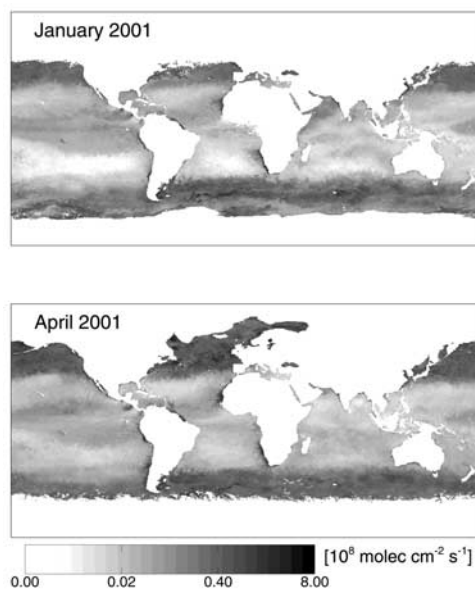
Figure 2. Marine isoprene fluxes (10^8 molecules cm^{-2} s^{-1}) for January and April 2001, shown on a 36 km^2 grid. Missing polar values reflect seasonal ice movement where satellite observations are unavailable. See color version of this figure in the HTML.

Table 1. Air-Sea Isoprene Flux Measurements (10^8 molec cm^{-2}s^{-1})

Data Set	Location	Date	Reported Data	MODIS (2001)
Bonsang et al. [1992]	NW Pacific	5, 1987	1.1	0.010
Milne et al. [1995]	Florida Straits	9, 1993	0.06–0.7	0.013
Broadgate et al. [1997]	1) North Sea[a]	1) 5, 1994	1) 0.47 (max)	1) 0.78 (max)
	2) Bellingshausen Sea	2) 11–12, 1992	2) 0.22 (mean)	2) 0.36 (mean)
Baker et al. [2000]	North Atlantic	5, 1997	0.08–0.6	0.080–0.71
Matsunaga et al. [2002]	NW PACIFIC	5, 2001	0.2–2.1	0.009–0.14

[a]MODIS data are unavailable 51–54°N; we use values from 55–60°N.

[1995] to estimate a 60 m ML and a mean ($\Delta C/\Delta Z$) of 0.32 nmol m^{-4}. The loss rate to the deeper ocean, L_{MIX}, at this location is then 3.2×10^2 molec cm^{-3}s^{-1}, which is insignificant compared to other losses; we assume this is true elsewhere. On sub-monthly timescales lateral advection and subduction also represent minor isoprene losses, with lifetimes >100s days (calculations not shown).

3. Air-Sea Fluxes

[11] MODIS global chlorophyll maps exhibit low concentrations in the gyres compared with higher concentrations in the margins and upwelling systems. Phytoplankton blooms are often seasonal events, the timing of which depends on light and nutrient availability, leading to considerable seasonal and interannual variability [*Gregg et al.*, 2003]. The largest blooms occur in spring when surface waters that incorporate nutrient-rich deep waters during winter mixing are stratified due to seasonal warming (e.g., MODIS 2001 Atlantic blooms: North in April; South in September).

[12] Figure 2 shows the calculated isoprene fluxes for January and April 2001. Fluxes range from 10^7–10^9 molecules cm^{-2}s^{-1}, which are comparable with published in situ flux measurements (Table 1). The underlying spatial pattern is similar to that for chlorophyll, consistent with air-sea exchange dominating the losses (Figure 1). The largest fluxes occur during the spring blooms. Coastal waters affected by upwelling and river runoff are also visible (e.g., western South Africa and Amazon outflow). Zonal values (Figure 1) are usually much less than the maximum values (Figure 2), reiterating the large variability in chlorophyll, and thus isoprene flux, over ocean basins.

[13] Table 1 lists the few published in situ flux measurements available to evaluate MODIS flux estimates; generally the values are of the same order of magnitude. Good agreement is found in the open North Atlantic [e.g.,

Broadgate et al., 1997; *Baker et al.*, 2000]. Large differences are observed in the Pacific [*Bonsang et al.*, 1992]. This may be due to a sensed optical depth shallower than typical chlorophyll maxima there, which can be >100 m. Coastal comparisons are poor [e.g., *Milne et al.*, 1995], but remotely sensed chlorophyll can be confounded in these areas by particulate material [*Carder et al.*, 2004]. Also, this study did not account for seaweed emissions that could lead to coastal underestimates [*Broadgate et al.*, 2004]. The worst comparisons are with measurements potentially influenced by terrestrial emissions [*Matsunaga et al.*, 2002]. Seasonal MODIS fluxes in the North Sea have an annual pattern matching the seasonal MODIS chlorophyll concentrations, but with the opposite seasonality of in situ flux measurements from a nearby site [*Broadgate*, 1995]; this is likely due to inaccuracies in the surface wind and chlorophyll retrievals at this coastal location. Clearly, oceanic isoprene cycling is not fully understood. It is unlikely that the MODIS instrument sampling time would affect the monthly mean flux values.

[14] Global marine isoprene emissions are estimated at 0.11 Tg isoprene/yr, and are fairly evenly distributed among all months (Table 2). This value is significantly less than previous estimates derived from sparse in situ data (1.2 Tg C/yr [*Bonsang et al.*, 1992] and 0.38 Tg C/yr [*Milne et al.*, 1995]), but closer to those derived from an annual measurement cycle (0.19 Tg C/yr [*Broadgate et al.*, 1997]).

4. Implications for Chemistry

[15] Previous modeling studies have noted the potential of marine hydrocarbon emissions to impact remote MBL photochemistry by affecting oxidation capacity [*Donahue and Prinn*, 1990; *Lewis et al.*, 2001]. Following *Lewis et al.* [2001] we quantify the relative role of marine isoprene fluxes in reducing remote MBL OH. The main OH sinks there include CO, CH$_4$, H$_2$, O$_3$, for which we assume concentrations of 60, 1700, 530, and 20 ppb (CO, CH$_4$, and H$_2$ values from Cape Grim surface

Table 2. Mean Hemispheric Marine Isoprene Fluxes Using 2001 MODIS Data[a]

	Flux, Tg/month			Flux, Tg/month	
Month	NH	SH	Month	NH	SH
Jan	0.004	0.005	Jul	0.002	0.004
Feb	0.004	0.005	Aug	0.002	0.008
Mar	0.005	0.005	Sep	0.002	0.010
Apr	0.005	0.005	Oct	0.003	0.008
May	0.004	0.004	Nov	0.003	0.008
Jun	0.003	0.003	Dec	0.003	0.006

[a]Annual global total = 0.11 Tg yr^{-1}.

observations, http://cdiac.esd.ornl.gov). We assume [OH] = 2×10^6 molecules cm^{-3}, and a MBL height of 100m. Typical isoprene fluxes estimated from MODIS in this locale are 5×10^8 molecules cm^{-2}s^{-1}. Using established reaction rate constants we estimate that marine isoprene emissions represent 1% of the main OH removal reactions in the remote MBL, in agreement with *Lewis et al.* [2001]. Additional sinks not considered here will only act to decrease further isoprene's role is reducing [OH].

5. Closing Remarks

[16] Many assumptions were made in the calculation of this marine isoprene flux inventory, each with uncertainties that are difficult to quantify. One is the applicability of the relationship between isoprene production rate and chlorophyll [*Shaw et al.*, 2003]. The phytoplankton tested were chosen to broadly represent typical oligotrophic, temperate, and bloom-forming species. For example, *Prochlorococcus sp.* solely accounts for >50% of the chlorophyll in tropical and sub-tropical oceans [*Liu et al.*, 1997]. However, in situ communities may not follow the same relationship or it may vary regionally. Much larger uncertainties likely come from our isoprene loss rate estimates. Biological isoprene consumption needs to be confirmed and quantified, and many relevant aqueous chemical properties are needed. The insufficiency of information precludes treating these losses regionally. Individual air-sea gas transfer models are also quite uncertain, and we estimate our choice could affect the fluxes by ±50%. Most importantly, there is a need for validation data as isoprene fluxes have been measured at only a few sites, to our knowledge only one with seasonal information. MODIS chlorophyll retrieval uncertainties, particularly over coastal and icy regions, can confound evaluation of the data. The effects of short-term light and temperature variations on isoprene production rates (~20% [*Shaw et al.*, 2003]) were not included in these monthly mean flux calculations because changes in biomass rather than physiology dominate chlorophyll concentrations on such time scales. However such variations could easily be included for shorter averaging periods.

[17] Our method of estimating global marine isoprene fluxes is a significant improvement over previous work based on either limited in situ measurements or proxy calculations using photochemical lability [*Guenther et al.*, 1995]. Several studies have shown indirectly that significant ocean emissions of reactive compounds are necessary to reconcile remote MBL measurements [e.g., *Singh et al.*, 2003]. A coupled atmosphere-ocean biogeochemistry model capable of accurately simulating such fluxes is clearly of great importance. Application of our method to other reactive compounds could provide zeroth-order a priori flux estimates for use with an inverse model approach to refine biogeochemistry models, provided there is a robust relationship between an ocean parameter (e.g., chlorophyll concentration) and the flux.

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