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Environmental and biological controls on seasonal patterns of isoprene above a rain forest in central Amazonia

Dandan Wei[a], Jose D. Fuentes[a,*], Tobias Gerken[a,c], Marcelo Chamecki[b], Amy M. Trowbridge[c], Paul C. Stoy[c], Gabriel G. Katul[d], Gilberto Fisch[e], Otávio Acevedo[f], Antonio Manzi[g], Celso von Randow[h], Rosa Maria Nascimento dos Santos[i]

[a] *Department of Meteorology and Atmospheric Science, The Pennsylvania State University, University Park, PA, USA*
[b] *Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, Los Angeles, CA, USA*
[c] *Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, MT, USA*
[d] *Nicholas School of the Environment, Duke University, Durham, NC, USA*
[e] *Aeronautical and Space Institute, Department of Science and Aerospace Technology, São Paulo, Brazil*
[f] *Universidade Federal de Santa Maria, Santa Maria, Rio Grande do Sul, Brazil*
[g] *Centro de Previsão de Tempo e Estudos Climáticos (CPTEC), Instituto Nacional de Pesquisas Espaciais (INPE), Cachoeira Paulista, São Paulo, Brazil*
[h] *National Institute for Space Research (INPE), São José dos Campos, São Paulo, Brazil*
[i] *Universidade do Estado do Amazonas, Manaus, Brazil*

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ABSTRACT

The Amazon rain forest is a major global isoprene source, but little is known about its seasonal ambient concentration patterns. To investigate the environmental and phenological controls over isoprene seasonality, we measured isoprene mixing ratios, concurrent meteorological data, and leaf area indices from April 2014 to January 2015 above a rain forest in the central Amazon, Brazil. Daytime median isoprene mixing ratios varied throughout the year by a factor of two. The isoprene seasonal pattern was not solely driven by sunlight and temperature. Leaf age and quantity also contributed to the seasonal variations of isoprene concentrations, suggesting leaf phenology was a crucial variable needed to correctly estimate isoprene emissions. A zero-dimensional model incorporating the estimated emissions, atmospheric boundary layer dynamics, and air chemistry was used to assess the contributions of each process on the variability of isoprene. Surface deposition was an important sink mechanism and accounted for 78% of the nighttime loss of isoprene. Also, chemical reactions destroyed isoprene and during 6:00 to 18:00 h local time 56, 77, 69, and 69% of the emitted isoprene was chemically consumed in June, September, December, and January, respectively. Entrainment fluxes from the residual layer contributed 34% to the early-morning above-canopy isoprene mixing ratios. Sensitivity analysis showed that hydroxyl radical (HO) recycling and segregation of isoprene–HO played relatively lesser roles (up to 16%) in regulating ambient isoprene levels. Nitric oxide (NO) levels dominated isoprene chemical reaction pathways associated with consumption and production of HO under low-NO and high volatile organic compound (VOC) conditions. While surface deposition and oxidative processes altered isoprene levels, the relative importance of these factors varied seasonally with leaf phenology playing a more important role.

1. Introduction

Among the biogenic volatile organic compounds, isoprene (C_5H_8, 2-methyl-1,3-butadiene) is the most abundantly emitted from the foliage of woody plant species. Its ecological function is still unclear, but current and prevailing consensus indicates that isoprene may act to increase the thermal protection of photosynthesis at high temperature (> 313 K) by either stabilizing the thylakoid membranes (Sharkey and Yeh, 2001) or quenching reactive oxygen species (Loreto and Velikova, 2001). The biosynthesis of isoprene is associated with the carboxylation process in the leaf chloroplast (Sharkey et al., 2008), and foliage temperature and intercepted photosynthetically active radiation (PAR) regulate emissions via stomata (Fall and Monson, 1992). Foliage temperature activates the enzyme responsible for isoprene biosynthesis (Monson and Fall, 1989) whereas PAR provides the energy to acquire the necessary carbon substrate to produce isoprene (Sharkey et al., 1991). Isoprene emissions occur only during the daytime and vary greatly with foliage phenology. Laboratory (Grinspoon et al., 1991) and

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[*] Corresponding author.
E-mail address: jdfuentes@psu.edu (J.D. Fuentes).

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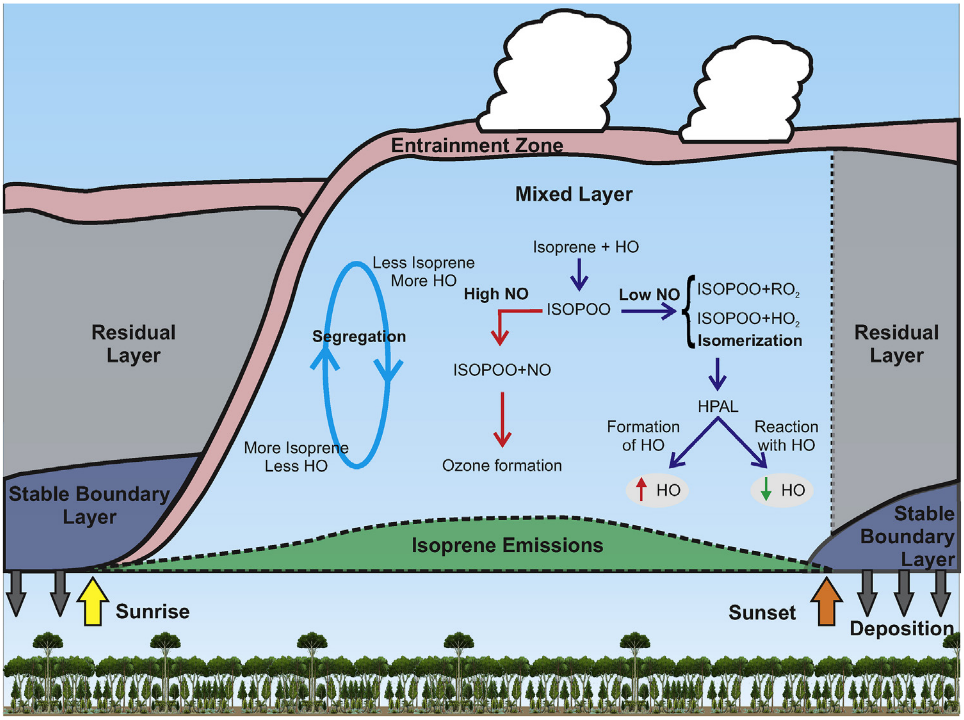

Fig. 1. Temporal variations of isoprene over the rain forest depend on emission, surface deposition, chemical transformation, and transport in (entrainment) and out (detrainment) of the atmospheric boundary layer. Each process differently contributes to ambient isoprene mixing ratios over the course of the day. After being emitted during the daytime, turbulence redistributes isoprene throughout the boundary layer while reactions with hydroxyl radicals (HO) decrease its concentration. Subsequent reaction pathways depend on nitric oxide (NO) levels. Under high NO conditions, ozone is generated while under low NO conditions notable amounts of HO can be recycled through isomerization of isoprene peroxy radicals (ISOPOO). Incomplete turbulent mixing slows down the reactions of isoprene with HO, and segregation of isoprene–HO can occur. Air entrainment from the free atmosphere into the mixed layer and deep boundary layer depths support rapid isoprene dilution, primarily during the morning when accelerated development of the convective boundary layer occurs. All these processes control the temporal patterns of isoprene mixing ratios above the rain forest. Figure modeled after Stull (1988).

field (Monson et al., 1994; Fuentes and Wang, 1999) studies demonstrate that leaves older than 2–4 weeks emit isoprene but younger leaves do not, even though they are competent to assimilate carbon dioxide (CO_2) (Fuentes et al., 1999; Wilkinson et al., 2009).

In this study we aim to (i) investigate the degree of seasonality in isoprene concentration using field experiments and (ii) identify the main processes explaining such seasonality via a zero-dimensional model that includes sources and sinks of isoprene as well as atmospheric boundary layer dynamics. Additional verifications on modeled links between ambient isoprene and its sources/sinks were conducted using diurnal concentration variations across different seasons. Once released from foliage, isoprene molecules can undergo surface deposition onto the plant canopy, can be oxidized, and can be transported into and out of the atmospheric boundary layer (ABL) (Fig. 1). Isoprene oxidation occurs via reactions with hydroxyl radical (HO), ozone (O_3), and nitrate radical (NO_3). Because of chemical reactions, isoprene molecules tend to reside in the atmosphere for just a few hours (Table 1).

Isoprene has a substantial impact on the chemistry of the atmosphere in the boundary layer overlying forested environments. The Amazon rain forest mostly experiences low levels of nitrogen oxides ($NO_x = NO + NO_2$). Occasionally, high NO_x levels are observed due to biomass burning (Gerken et al., 2016). Under higher NO_x conditions, isoprene oxidation processes contribute to the formation of O_3 (Kuhn et al., 2007). In addition, products of isoprene photooxidation are important precursors to secondary organic aerosols (SOA), particularly in the rain forest where isoprene is abundantly produced year round (Claeys et al., 2004; Paulot et al., 2009b; Surratt et al., 2009). Because SOAs can grow sufficiently large to activate and become cloud condensation nuclei (CCN) and scatter and absorb solar irradiance, they play critical roles in weather and climate (Pöschl et al., 2010). Also, theoretical and experimental studies (Taraborrelli et al., 2012; Fuchs et al., 2013) indicate that the photooxidation of isoprene may contribute to appreciable amounts of HO recycling. In environments such as the rain forest, isoprene plays a central role in sustaining the oxidation capacity of the lower atmosphere by adjusting HO levels (Lelieveld et al., 2008; Nölscher et al., 2016). Hence, it is necessary to estimate seasonal emission rates, ambient levels, and oxidation rates of isoprene in the tropical rain forest to establish regional SOA and HO budgets, and to develop an improved understanding of the role of rain forests in the Earth system.

Table 1
Isoprene chemical lifetimes with respect to assumed mixing ratios (in parts per billion on a volume basis, ppbv) of hydroxyl radical, ozone, and nitrate radical.

Oxidant	Rate coefficient[a] (cm^3 $molecule^{-1}$ s^{-1})	Mixing ratio (ppbv)	Chemical lifetime (h)
Hydroxyl radical	1.0×10^{-10}	1.0×10^{-4}	1
Ozone	1.28×10^{-17}	20.0	44
Nitrate radical	6.86×10^{-13}	5.0×10^{-3}	3

[a] Reaction rate coefficients are from Atkinson (1997) at temperature of 298 K.

Tropical rain forests experience year-round high temperature and PAR levels and may thus be assumed to support minor seasonality in isoprene emissions (Levis et al., 2003). However, strong seasonality in ambient isoprene levels is observed over the Amazon rain forest (Kesselmeier, 2002; Kuhn et al., 2004). Studies on tropical tree species show mature leaves exhibit higher isoprene emissions than new leaves (2 *versus* 30–40 $nmol\,m^{-2}\,s^{-1}$; Figure 4b in Jardine et al., 2016). Also, remote sensing studies (Barkley et al., 2008) in the Amazon basin demonstrate that variations in leaf area and enhanced vegetation indices (EVI) before the dry season are consistent with observed decreases in the slant atmospheric columns of formaldehyde (HCHO, Palmer et al., 2007), which is a high-yield product of isoprene oxidation and is assumed as a proxy for isoprene emissions (Palmer et al., 2006). Such results suggest large-scale reductions in isoprene biosynthesis due to new leaf growth prior to the dry season. While co-located seasonal isoprene and phenology measurements are not available for the Amazon rain forest, close links exist between phenology and photosynthesis (Wu et al., 2016), which would be consistent with the observed seasonality in isoprene emissions. Previous ecosystem-level studies in the tropical rain forest (Rinne et al., 2002; Greenberg et al., 2004; Karl et al., 2004; Kuhn et al., 2007; Rizzo et al., 2010; Jardine et al., 2012) were performed during brief periods and confirmed