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Seasonality of isoprene emissions and oxidation products above the remote Amazon†

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The Amazon rainforest is the largest source of isoprene emissions to the atmosphere globally. Under low nitric oxide (NO) conditions (*i.e.* at NO mixing ratios less than about 40 pptv), isoprene reacts rapidly with hydroxyl (OH) to form isoprene-derived peroxy radicals (ISOPOO), which subsequently react with the hydroperoxyl radical (HO₂) to form isoprene epoxydiols (IEPOX). IEPOX compounds are efficient precursors to the formation of secondary organic aerosols (SOA). Natural isoprene emissions, therefore, have the potential to influence cloudiness, rainfall, radiation balance and climate. Here, we present the first seasonal analysis of isoprene emissions and concentrations above the Amazon based on eddy covariance flux measurements made at a remote forest location. We reveal the forest to maintain a constant emission potential of isoprene throughout the year (6.9 mg m⁻² h⁻¹). The emission potential of isoprene is calculated by normalising the measured fluxes to a set of standard conditions (303 K and 1500 μmol m⁻² s⁻¹). During the wet season a factor of two reduction in absolute emissions was observed but this is explained entirely on the basis of meteorology and leaf area index, not by a change in isoprene emissions potential. Using an innovative analysis of the isoprene fluxes, in combination with measurements of its oxidation products and detailed chemical box-modelling, we explore whether concentrations of IEPOX follow the same seasonal cycle as the isoprene precursor. Our analysis implies that during the dry season (Sep–Jan) air pollution from regional biomass burning provides a modest increase in NO concentrations (indirectly inferred from a combination of other anthropogenic tracer measurements and box-modelling) which creates a competing oxidation pathway for ISOPOO; rather than forming IEPOX, alternative products are formed with less propensity to produce aerosol. This competition decreases IEPOX formation rates by a factor of two in the dry season compared with a scenario with no anthropogenic NO pollution, and by 30% throughout the year. The abundance of biogenic SOA precursors in the Amazon appears not to be dictated by the seasonality of natural isoprene emissions as previously thought, but is instead driven by regional anthropogenic pollution which modifies the atmospheric chemistry of isoprene.

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Environmental significance

We demonstrate the Amazon rainforest to maintain a constant isoprene emission potential, with the factor of two reduction in emission observed during the wet season explained entirely by meteorology and leaf area. Although isoprene emission rates are twice as large in the dry season, we suggest that widespread biomass burning at this time leads to modest increases in NO, which serves to suppress the formation of isoprene epoxydiol (IEPOX) secondary organic aerosol precursors by up to a factor of two. Rather than reacting with HO₂ to form IEPOX, the isoprene peroxy radicals have an increased opportunity to react with NO. Therefore, the seasonal cycle in aerosol precursors in Amazonia is regulated, not by the availability of isoprene, but by anthropogenic biomass burning.

1. Introduction

The Amazon rainforest is a globally important source of isoprene,^{1–3} yet only a few, short-term emission measurements of this reactive compound exist. These provide a tantalizing but narrow insight into the diurnal and seasonal dynamics of isoprene emission from the rainforest canopy, and its impact on atmospheric chemistry.^{4–9} Even less is known about how isoprene emissions might change as the forest transitions between the wet and dry seasons and what impact this might have on isoprene-derived SOA precursors such as IEPOX. Satellite observations of formaldehyde (HCHO), a second generation oxidation product of isoprene, have previously been used to probe seasonal isoprene emission dynamics indirectly.¹⁰ Barkley *et al.* (2009)¹¹ showed that HCHO column density measured above the Amazon rainforest exhibits a clear and robust seasonal cycle, with lower HCHO amounts detected in the wet season and higher amounts in the dry season. This pattern reflects the metabolic processes that control the production of isoprene synthase, which are closely linked to photosynthesis and hence to light and temperature.¹² However, this analysis also showed a marked dip in HCHO amounts in the transitional period between the wet and dry seasons, alluding to further controls. They postulated that the near absence of HCHO above background levels at this time was either due to a shutdown in isoprene emissions, caused by a wide-scale seasonal leaf flushing event, or to a dramatic decrease in the concentrations of the hydroxyl radical (OH), the primary chemical isoprene oxidant in the atmosphere.

Understanding of isoprene oxidation chemistry has evolved rapidly in the last decade, with numerous laboratory and theoretical studies exploring in detail the key degradation pathways and branching ratios involved.^{13–17} Under pristine conditions (*i.e.* concentrations of NO < ~40 pptv), isoprene reacts with OH to form a range of peroxy radical species (ISOPOO) which can react with HO₂ radicals to produce isoprene hydroxyhydroperoxides (ISOPOOH).¹⁴ ISOPOOH can be further oxidised by OH to form lower volatility epoxydiols (IEPOX), which have been shown to efficiently condense onto pre-existing aerosol and so contribute mass to secondary organic aerosols (SOA)^{17–20} (see Section 9 of ESI†).

In more polluted environments, NO emitted from anthropogenic combustion processes (*e.g.* fossil fuel combustion and biomass burning) provides a competing reaction pathway for the ISOPOO radicals,²¹ resulting in the formation of greater amounts of methyl vinyl ketone (MVK) and methacrolein (MACR), as well as HCHO, glyoxal and methacrylic acid epoxide (MAE). These all give lower yields of SOA precursors than IEPOX²² under the temperature regime of the tropical forest.²³ Previous field measurements of these species/processes in the

Amazon rainforest have only been conducted downwind of the city of Manaus (*ca.* 2.1 million inhabitants) and are limited to the wet season.^{24,25} A detailed long-term study of isoprene emissions and its oxidation under remote conditions and through different seasons is still lacking.

To improve understanding of the sources and fate of isoprene in Amazonia, we measured the surface-atmosphere exchange of isoprene and the sum of its oxidation products (MVK + MACR + ISOPOOH, collectively termed Iso_{ox}) with hourly resolution using a proton transfer reaction mass spectrometer (PTR-MS)²⁶ for an eleven month period at a remote site in the central region of the Amazon rainforest. We use this unique data set to reveal the seasonal dynamics of both isoprene emissions and its oxidation chemistry above the Amazon biome.

2. Results

Monthly average daytime (09:00–17:00 local time) isoprene concentrations and fluxes are shown in Fig. 1A and B respectively. A seasonal cycle is evident with both concentrations and fluxes largest during the dry season and up to a factor of two lower during the wet season. Fig. 1C shows the monthly and annual average isoprene emission potentials, which are calculated by normalising the measured fluxes to a set of standard conditions (303 K and 1500 μmol m^{–2} s^{–1}) (see Section 2 of ESI†).²⁷ Monthly values (except November and March, when data were limited and uncertainty large) deviate only very slightly and are statistically not significantly different from the annual average of 6.9 mg m^{–2} h^{–1}. This demonstrates that the rainforest maintains a constant isoprene emission potential throughout the year and that the seasonal cycle in observed emission rates and ambient concentrations can be explained by fluctuations in light, temperature and leaf area index. It is, therefore, not necessary to invoke changes in the emission potential caused by phenomena such as leaf flushing or mass flowering events or changes in phenology⁸ to explain the observed seasonality in isoprene emission rates at this site. These measurements also provide, for the first time, direct unequivocal evidence that isoprene fluxes in Amazonia do not substantially decrease during the transitional period between wet and dry seasons.

In order to investigate potential seasonality in isoprene photochemistry we derived the relative abundance of the major oxidation products of isoprene, MVK + MACR and ISOPOOH (Iso_{ox}). ISOPOOH reacts on the metal surfaces within the PTR-MS sampling and analysis system (*e.g.* inlet lines, capillary and drift tube) and is converted to MVK. As a result, Iso_{ox} can be measured directly as the sum of species detected at *m/z* 71 by



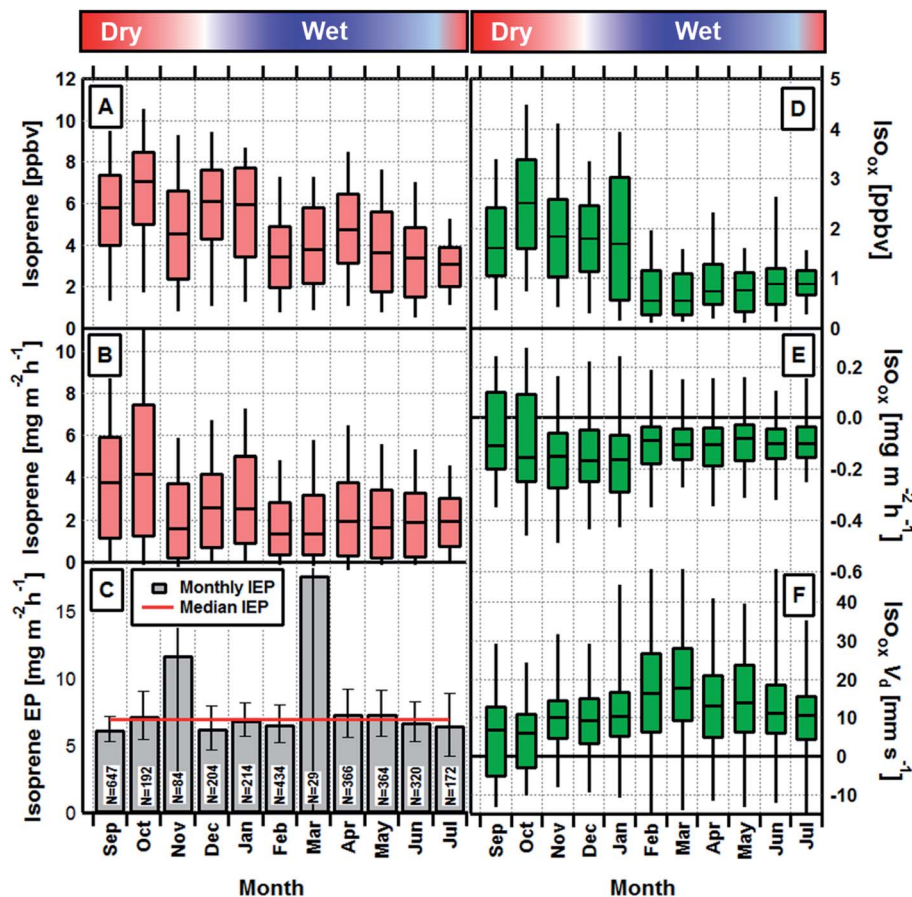


Fig. 1 Box and whisker plots (centre line, median; box limits, upper and lower quartiles; whiskers, 10th and 90th percentiles) showing the monthly mean daytime (09:00 to 17:00 local) isoprene concentrations (A) and fluxes (B) measured above the rainforest, in relation to the wet–dry seasonality. Panel (C) shows the isoprene fluxes normalised to standard conditions (see text) to give the isoprene emission potential (IEP) of the forest. *N* = number of observations. Error bars show $\pm 1\sigma$ of calculated emission potentials. Panels (D–F) show the concentration, flux and deposition velocities, respectively, for the isoprene oxidation products MVK, MACR and ISOPOOH, which we collectively term Iso_{ox}.

the PTR-MS.²⁸ The exact conversion efficiency within our instrument is not known, but the long inlet line (>50 m) and steel capillary combined with a lack of signal at the ISOPOOH parent *m/z* suggest conversion was at or close to 100%.

Iso_{ox} concentrations and fluxes and its derived deposition velocity ($V_d = -\text{flux}/\text{concentration}$) are shown in Fig. 1D–F, respectively. The seasonal cycle in monthly average concentrations of Iso_{ox} (Fig. 1D) broadly follows that of isoprene but is enhanced further due to changes in the deposition process, as implied by the larger deposition velocity, between February and May (Fig. 1F).

Resistance analysis (see Methods) allows the total deposition resistance ($R_t = 1/V_d$) to be decomposed into the component resistances describing atmospheric transport (aerodynamic resistance, R_a and boundary layer resistance, R_b) and the interaction with the canopy (R_c). Fig. 2 shows a clear seasonal cycle in R_t (and thus V_d), which is driven almost entirely by variations in the canopy resistance, with R_a and R_b relatively constant throughout the year. This can be related to a change in the relative abundance of the three components of Iso_{ox}. Previous deposition measurements of ISOPOOH + IEPOX above

a temperate forest suggest a near zero R_c .²⁹ This is due to the rapid conversion of ISOPOOH to MVK upon contact with leaf surfaces and subsequent conversion to methyl ethyl ketone (MEK).³⁰ In contrast, MVK + MACR deposits with an R_c value of at least 50 s m^{−1}, as implied by the January measurements in Fig. 2. Utilizing the strongly contrasting canopy resistances of these compounds, we can estimate the fraction of ISOPOOH detected at *m/z* 71 as:

$$f_{\text{ISOPOOH}} = \frac{V_{d(s)} - V_{d(s)\text{MVK+MACR}}}{V_{d(s)\text{ISOPOOH}} - V_{d(s)\text{MVK+MACR}}}, \quad (1)$$

where $V_{d(s)}$ is the measured deposition velocity of Iso_{ox} and $V_{d(s)\text{MVK+MACR}}$ and $V_{d(s)\text{ISOPOOH}}$ are the deposition velocities of MVK + MACR and ISOPOOH, respectively. Because the aerodynamic resistance is in part height dependent, here we use deposition velocities that have been extrapolated to the surface (*s*)

(e.g. $V_{d(s)} = \frac{1}{\left(\frac{1}{V_d(z-d)}\right) - R_a(z-d)}$). For ISOPOOH, where the value of R_c is expected to be at, or close to, zero, the $V_{d(s)}$ can be given as $1/R_b$, equal to 4.5 cm s^{−1}. Determining the deposition





Fig. 4 The output from the Master Chemical Mechanism box modelling study which calculated the ratio of ISOPOOH to MVK + MACR production rates (χ) for a range of NO concentrations (a) and the corresponding reactive loss to be expected to each of the four degradation pathways f_{NO} , f_{HO_2} , f_{RO_2} and f_{ISOM} (b). The box model was initialised for the average conditions of the month of September, where the measured isoprene concentration was 5.8 ppbv. Equivalent plots were made for the other 10 months of the study. The production ratio uncertainties are discussed in Section 4 and the ESI (Section 6.2†).

fractional contribution of the four reaction pathways for ISOPOO, f_{HO_2} , f_{NO} , f_{RO_2} and f_{ISOM} over the same range of NO concentrations. Using an equivalent of these two plots for each month as a lookup table, we estimated the fraction of ISOPOO that reacts *via* the main HO_2 and NO pathways as well as the contributions from peroxy radical (RO_2) cross and self-reactions³² and isomerisation pathways^{16,33,34} over the 11 months measurement period. The results of this exercise are shown in Fig. 5a together with the average concentrations of BC and acetonitrile.

The box model results suggest that HO_2 accounts for 46% of the reactive loss of ISOPOO over the year, consistent with the view that HO_2 is the principal ISOPOO sink in the Amazon, especially under the clean, low NO, conditions of the wet season when its contribution peaked at 53%.^{14,34} By comparison, the NO pathway accounts for between ~28 and 54% of the ISOPOO reactive loss, with an average contribution of 37% over the year. The NO pathway is largest during September and January (the dry season) when increased deforestation activities and agricultural practices result in biomass burning plumes containing elevated concentrations of NO. These plumes are advected throughout the Amazon rainforest.^{35,36} Rainforest soils also act as a minor source of NO and these emissions may exhibit some seasonal cycle.³⁷ However, the strong association between the NO pathway and both black carbon and acetonitrile, two tracers of biomass burning that are independent of soil emissions, suggests that locally produced NO cannot be the principal driver for the observed pattern. An analysis of terrestrial fire counts and brightness retrieved by the Terra MODIS satellite along calculated back trajectories confirms that biomass burning is

the most likely dominant source of the measured BC and acetonitrile concentrations (see Section 8 of the ESI†).

To relate our results to current understanding, we additionally ran the GEOS-Chem global chemical transport model over the same period for the grid square coincident with our measurement site (see Section 5.3 of the ESI†). Concentrations of NO in the model were relatively constant (28 pptv) across the 11 months period, with an even split between anthropogenic (EDGAR v4.2) and natural emissions (GFED Version 4). The resulting $f_{\text{NO}}/f_{\text{HO}_2}$ ratio was approximately unity throughout the year, which suggests the seasonal influence from biomass burning is not well captured within the model.

3. Discussion

The isoprene emissions dataset presented here shows, for the first time, that the seasonal cycle in isoprene emissions in Amazonia is controlled purely by variations in meteorology and leaf area, and that the emission potential of the forest remains rather constant throughout the seasons. This implies that the inability of chemical transport models to reconcile isoprene concentrations during the wet-to-dry transition points towards uncertainty in chemistry rather than in the modelled isoprene emission rates. This is consistent with the findings of Wells *et al.* (2020) who attribute the discrepancies in satellite-derived isoprene concentrations with model estimates to underestimates in NO concentrations, which bias modelled OH concentrations.³⁸ Our measurements further support this conclusion, with NO concentrations ranging between 40 and 145 pptv required to obtain our derived production ratios in the chemical

details of the other 10 months shown in Section 6.2 of the ESI†. Although the absolute production ratio is uncertain, any error is applied systematically to each point and, therefore, the seasonal pattern is unaffected. In contrast, changes in OH concentration across the seasons could directly affect the production ratio calculated for each month (e.g. $k_{i,OH}$). A sensitivity analysis, where $k_{i,OH}$ was varied following the seasonal pattern of OH implied by isoprene flux to concentration ratios, shows changing OH concentrations to have a relatively minor impact on the estimated production rates (6% increase overall), with the largest difference noted for September, where the production rate increased by 15%. Even then, when accounting for variability in the OH concentrations, the seasonal pattern in ISOPOO reactive loss remained consistent (see Section 6.1 of the ESI†).

Liu *et al.* (2016)²⁴ reported direct observations of ISOPOOH to MVK + MACR production ratios at a different site (T3) within the Amazon basin during March 2014, using a more direct measurement approach, with observed values ranging between 0.6 and 0.9. Their site was closer to Manaus and experiences, at least at times, higher pollution (*i.e.* higher [NO]) than the ZF2 site used in this study, which would lower production ratios in favour of MVK + MACR. Our production ratio for March of the same year was 0.98, (0.91 to 1.18), falling just outside the range reported by Liu *et al.*, providing a useful ground-truthing for our approach.

A further limitation of our study is the absence of NO measurements, which would provide confirmation that the changes in calculated production ratios reflect the availability of NO. A comparison of BC and NO measurements made between February 2014 and June 2015 at the T3 site, showed a clear relationship between the two species on a timescale of days to months (see Section 1.4 of the ESI†). This confirms that black carbon concentrations can offer a qualitative assessment of the anthropogenic trend in NO in Amazonia despite the very different chemical lifetimes of these two species. The fact that Fig. 3 shows such a close relationship between derived production ratios and two well-known markers of biomass burning provides confidence that our approach can broadly represent the trends in isoprene oxidation chemistry at this site. In addition, the average monthly NO concentrations implied from the ISOPOOH to MVK + MACR production ratios, ranged between 41 pptv (March) and 139 pptv (October), which compare well with previous background NO concentrations reported above the Amazon (15 to 80 pptv (ref. 24, 42 and 43)) providing a further sanity check for our results. Nonetheless, future work is required to better quantify the complex role that anthropogenic pollution plays in mediating isoprene chemistry and SOA formation in the remote Amazon. Recent advances in online mass spectrometry mean it is now possible to measure the major isoprene oxidation products, including both ISOPOOH and IEPOX, directly. Combining long-term ground based measurements of these species together with direct observations of NO should now become a priority, so the true impact that human pollution has in this remote part of the world can be further established.

5. Conclusions

Our findings shed light on the seasonal dynamics of both isoprene emissions from the tropical rainforest of Amazonia and its chemical fate. They confirm the tropical rainforest to maintain a constant isoprene emission potential throughout the year, with seasonal changes in emission rates explained by the latest isoprene emission algorithms on the basis of light temperature and leaf area index.

The deposition rates of isoprene oxidation products, when explored to their fullest, hint at broad trends in the chemical fate of isoprene that are driven by anthropogenic pollution, specifically by nitric oxide. They indicate that reaction with HO₂ is the dominant mechanistic pathway for isoprene peroxy radical oxidation in the remote Amazon, accounting for an average of 46% of the reactive loss of ISOPOO throughout the year, but that ISOPOO chemistry is sensitive to the level of NO present, with its oxidation pathways shifting towards reaction with NO during the dry season, when regional biomass burning is at its highest. This competition decreases IEPOX formation rates by a factor of two in the dry season compared with a scenario with no anthropogenic NO pollution, and by 30% throughout the year, despite absolute emissions of isoprene being a factor of two larger at this time. We conclude that the abundance of this important isoprene SOA precursor in the Amazon is, therefore, not dictated by the seasonality of natural isoprene emissions as previously thought, but instead, is strongly mediated by regional anthropogenic pollution.

6. Materials and methods

6.1 Flux measurements

Sample air was drawn from an inlet mounted at a height of 38 m on the triangular tower TT34 at the LBA ZF2 measurement site (2.594637° S, 60.209519° W, altitude 67 m) located in the Reserva Biológica do Cueiras in Central Amazonia, Brazil (see Section 1 of ESI†). Flux measurements were made using the virtual disjunct eddy covariance (vDEC) technique, in which a covariance function between vertical wind velocity measurements (w) and VOC mixing ratios (c) is used to determine the flux for each selected compound (F_c), such that

$$F_c(\Delta t) = \frac{1}{n} \sum_{i=1}^n w' \left(i - \frac{\Delta t}{\Delta t_w} \right) c'(i), \quad (3)$$

where prime denotes the deviation of the instantaneous value from its 45 min mean vertical wind component or concentration. Δt refers to the time-lag between the concentration measurement and the vertical wind velocity measurement which results from the spatial separation between sonic anemometer and PTR-MS. Δt_w is the sampling interval of the vertical wind velocity measurements (*i.e.* 0.1 s) and n gives the number of samples (approx. 1350), which are in effect disjunct due to the sequential and discontinuous sampling of the PTR-MS, from each 45 min averaging period. The remaining 15 minutes of each hour were used for a five minute background measurement at the selected ions and dwells corresponding to



each of the four degradation pathways: reaction with NO, reaction with HO₂, reaction with RO₂, and isomerization, and (b) to investigate the sensitivity of HCHO and IEPOX production from isoprene photooxidation to the NO concentration, under a range of conditions representative of the observations.

The complete isoprene degradation mechanism in MCM v3.3.1 consists of 1926 reactions of 602 closed shell and free radical species, which treat the chemistry initiated by reaction with OH radicals, NO₃ radicals and ozone. It contains much of the isoprene HO_x recycling chemistry identified as important in recent years under “low NO” conditions, including the peroxy radical 1,5 and 1,6 H-shift chemistry described in the LIM1 mechanism,^{16,51} as summarized in Wennberg *et al.* (2018)¹³ Model photolysis rates were calculated using the Tropospheric Ultraviolet and Visible Radiation Model (TUV v5.2).⁵²

Author contributions

EN, CNH, ARM, BL and PA devised the project. EH, AV, BD, AMYS, JB, BL and MDS conducted the field measurements. BL and EH analysed the flux data. MJN, ARR and EM conducted the modelling work. MPB and EC analysed the satellite data and AV and BL analysed back trajectories. BL, EN, CNH, ARR and NJM wrote the manuscript with contributions from all co-authors.

Conflicts of interest

The authors declare no competing interests

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