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Influence of urban pollution on the production of organic particulate matter from isoprene epoxydiols in central Amazonia

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Abstract

The atmospheric chemistry of isoprene contributes to the production of a substantial mass fraction of the particulate matter (PM) over tropical forests. Isoprene epoxydiols (IEPOX) produced in the gas phase by the oxidation of isoprene under HO_2-dominant conditions are subsequently taken up by particles, thereby leading to production of secondary organic PM. The present study investigates possible perturbations to this pathway by urban pollution. The measurement site in central Amazonia was located 4 to 6 hours downwind of Manaus, Brazil. Measurements took place from February through March 2014 of the wet season, as part of the GoAmazon2014/5 experiment. Mass spectra of organic PM collected with an Aerodyne Aerosol Mass Spectrometer were analyzed by positive-matrix factorization. One resolved statistical factor ("IEPOX-SOA factor") was associated with PM production by the IEPOX pathway. Loadings of this factor correlated with independently measured mass concentrations of tracers of IEPOX-derived PM, namely C_5-alkene triols and 2-methyltetrols (R = 0.96 and 0.78, respectively). Factor loading, as well as the ratio of the factor loading to organic PM mass concentration, decreased under polluted compared to background conditions. For the study period, sulfate concentration explained 37% of the variability in the factor loading. After segregation of the data set by NO_y concentration, the sulfate concentration explained up to 75% of the variability in factor loading within the NO_y subsets. The sulfate-detrended IEPOX-SOA factor loading decreased by two- to three-fold for an increase in NO_y concentration from 0.5 to 2 ppb. The suppressing effects of elevated NO dominated over the enhancing effects of higher sulfate with respect to the production of IEPOX-derived PM. Relative to background conditions, the Manaus pollution contributed more significantly to NO_y than to sulfate. In this light, increased emissions of nitrogen oxides, as anticipated for some scenarios of Amazonian economic development, could significantly alter pathways of PM production that presently prevail over the tropical forest, implying changes to air quality and regional climate.

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1. Introduction

Organic compounds comprise up to 90% of the mass concentration of submicron organic particulate matter (PM) over tropical forests (Kanakidou et al., 2005). Submicron PM has adverse effects on human health (Nel, 2005; Pope III and Dockery, 2006) and influences air quality and climate by scattering radiation and acting as cloud condensation nuclei (Ramanathan et al., 2001; Kaufman et al., 2002). A significant fraction of the submicron organic material originates from secondary processes, mainly by the atmospheric oxidation of volatile organic compounds (VOCs) emitted as part of natural and human activities (Zhang et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009). The particle life cycle over Amazonia is in particular strongly influenced by secondary processes that produce organic PM (Martin et al., 2010a; Pöschl et al., 2010). Biogenic emissions from tropical forests are high, and environmental conditions favor photooxidation reactions. The reactive chemistry and the relative importance of pathways leading to PM production can be strongly guided by regulating species, such as sulfate and nitric oxide (Surratt et al., 2007a; Worton et al., 2013; Liu et al., 2016a). The concentrations of these species depend on their background occurrence, pollution sources, and the relative mix of background and polluted air masses.

Over tropical forests such as Amazonia, the atmospheric chemistry of isoprene produces a substantial fraction of the submicron organic PM (Chen et al., 2009; Robinson et al., 2011; Chen et al., 2015; Isaacman-VanWertz et al., 2016). Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the non-methane VOC most abundantly emitted by tropical forests (Guenther et al., 2012), and isoprene epoxydiols (IEPOX) have been identified as important intermediates in the production of PM from isoprene (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012). A chemical sequence for the production of IEPOX-derived PM from the photooxidation of isoprene in the

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atmosphere is represented in Figure 1. The sequence is initiated when isoprene peroxy radicals (ISOPOO) are produced in the gas phase by reactions between isoprene and photochemically generated hydroxyl radicals (OH). The reactive fate of the ISOPOO radicals can differ under background compared to polluted conditions (Surratt et al., 2010; Crounse et al., 2011; Worton et al., 2013).

Under background conditions, meaning that HO_2 pathways are favorable in the absence of extensive NO pollution (Wennberg, 2013; Liu et al., 2016a), the ISOPOO radicals continue in large part through the series of species highlighted in yellow in Figure 1. Through HO_x-facilitated reaction steps, the ISOPOO radicals produce hydroperoxides (ISOPOOH) as major first-generation products and subsequently isoprene epoxydiols (IEPOX) as major second-generation products (Carlton et al., 2009; Paulot et al., 2009; Liu et al., 2013; St. Clair et al., 2015; Liu et al., 2016a). Some of the produced IEPOX undergoes reactive uptake to particles, as facilitated by hydronium ions at the surface (Surratt et al., 2007a; Lin et al., 2012; Gaston et al., 2014; Kuwata et al., 2015; Lewandowski et al., 2015). This chemical sequence can contribute a significant fraction of submicron PM mass concentration over tropical forests (Claeys et al., 2004; Hu et al., 2015). Laboratory studies indicate that about half of the PM produced by isoprene photooxidation under HO_2-dominant conditions in the presence of acidic sulfate particles is associated with IEPOX production and uptake (Liu et al., 2015). Interaction of IEPOX with cloud waters warrants investigation (Lim et al., 2005; Ervens et al., 2011; Budisulistiorini et al., 2015; Chen et al., 2015). In addition to IEPOX pathways, laboratory studies suggest that multifunctional hydroperoxides produced in the gas phase can contribute to isoprene-derived PM production (Krechmer et al., 2015; Liu et al., 2016b; Riva et al., 2016b).

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After reactive uptake of IEPOX, particle-phase reactions can produce several different families of species. These species are collectively labeled "IEPOX-derived PM" and represent a subset of the ambient organic PM, as labeled in Figure 1. The presence of 2-methyltetrols, C_5-alkene triols, 3-methyltetrahydrofuran-3,4-diols, organosulfates, and related oligomers in ambient PM is an indicator of PM production by IEPOX uptake under atmospheric conditions (Claeys et al., 2004; Surratt et al., 2006; Surratt et al., 2007b; Surratt et al., 2010; Robinson et al., 2011; Lin et al., 2012; Lin et al., 2014). Even though these species may differ in some cases from the actual compounds in the atmospheric PM due to thermal decomposition during analysis (Lopez-Hilfiker et al., 2016), they serve as chemical tracers for the atmospheric concentration of IEPOX-derived PM (Hu et al., 2015; Isaacman-VanWertz et al., 2016). The analytical methods highlighted in Figure 1, including that of the "IEPOX-SOA factor" of the AMS analysis used herein, can lead to over- and underestimated IEPOX-derived PM concentrations. This uncertainty is represented in the figure by the brown dashed lines that approximately but not exactly correspond to IEPOX-derived PM.

Under polluted conditions, the reactive sequence of isoprene and ultimately PM production can become significantly altered (Figure 1). NO concentrations can be sufficiently high that ISOPOO radicals react almost entirely with NO in place of HO_2, thereby largely producing methacrolein (MACR) and methyl vinyl ketone (MVK) in place of ISOPOOH (Liu et al., 2016a). As a result, IEPOX production can be greatly decreased, ultimately reducing PM production by IEPOX pathways. A minor channel along the NO pathway can still produce IEPOX, although much less efficiently (Jacobs et al., 2014). Under NO-dominant conditions, alternative pathways of PM production can become active, though in lower yields. MACR can be oxidized to produce peroxymethylacrylic nitric anhydride (MPAN), which is a precursor to

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methacrylic acid epoxide (MAE) and hydroxymethylmethyl-α-lactone (HMML), and these compounds can undergo reactive uptake to produce PM (Kjaergaard et al., 2012; Lin et al., 2013; Worton et al., 2013; Nguyen et al., 2015). Glyoxal produced from isoprene oxidation can contribute to PM production (Volkamer et al., 2007; Ervens and Volkamer, 2010; McNeill et al., 2012; Marais et al., 2016).

Another possible mechanism affecting PM production by IEPOX uptake under polluted conditions is altered particle composition, especially particle acidity, largely driven by sulfate. Laboratory studies show that IEPOX uptake increases with increasing acidity (Gaston et al., 2014; Kuwata et al., 2015; Liu et al., 2015). A proposed reaction during uptake is the acid-catalyzed ring opening of the IEPOX molecule (Surratt et al., 2010). The subsequent particle-phase reactions include the addition of available nucleophiles, such as water to produce tetrols or sulfate to produce organosulfates as well as their oligomers (Surratt et al., 2010; Lin et al., 2014; Nguyen et al., 2014). In support of this proposed mechanism, analyses by positive-matrix factorization (PMF) of mass spectra collected in the southeastern USA identified PMF factors associated with IEPOX-derived PM, and these factors correlated positively with sulfate mass concentrations (Budisulistiorini et al., 2013; Hu et al., 2015; Xu et al., 2015). In short, different regimes of NO:HO_2 concentration ratios and different possible PM compositions between polluted and background conditions can lead to different product distributions and different production rates of IEPOX-derived PM.

The extent to which pollution may shift the production pathways of IEPOX-derived PM over tropical forests remains to be elucidated. The study described herein is based on data sets collected in the wet season downwind of Manaus, Brazil, during the *Observations and Modeling of the Green Ocean Amazon* Experiment (GoAmazon2014/5) (Martin et al., 2016c). The research

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site was influenced at times and to variable extents by the pollution outflow from the Manaus metropolitan area. Compared to the background environment in Amazonia, the Manaus plume had high number concentrations of particles and enhanced concentrations of pollutants, including oxides of nitrogen and sulfate (Kuhn et al., 2010; Martin et al., 2016c). The reactive gas-phase chemistry was strongly guided by the relative mix of background and polluted air masses (Trebs et al., 2012; Liu et al., 2016a). The analysis herein focuses on how the pollution perturbed IEPOX-derived PM production relative to background conditions.

2. Methodology

Data sets were collected at the "T3" site (3.2133 °S, 60.5987 °W) located 70 km to the west of Manaus, Brazil, in central Amazonia (Martin et al., 2016c). The site was situated in a pasture (2.5 km × 2 km) surrounded by forest. The analysis herein focuses on data sets collected during the wet season period of February 1 to March 31, 2014, corresponding to the first Intensive Operating Period (IOP1) of the GoAmazon2014/5 experiment.

A High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, hereafter AMS; Aerodyne, Inc., Billerica, Massachusetts, USA) recorded the primary data set of this study. The AMS provided quantitative bulk characterization of atmospheric PM at a time resolution of minutes. The design principles and capabilities of this instrument are described in the literature (DeCarlo et al., 2006; Canagaratna et al., 2007). The instrument was housed within a temperature-controlled research container, and the inlet to the instrument sampled from 5 m above ground level. Detailed aspects of AMS operation are presented in the Supplement (Section S1). In brief, ambient measurements were obtained for every 4 of 8 min. Organic, sulfate, ammonium, nitrate, and chloride PM mass concentrations were obtained from "V-mode" data. The choice of ions to fit was aided by the "W-mode" data, which were collected once every five

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days. Data analysis was performed using *SQUIRREL* (1.56D) and *PIKA* (1.14G) of the AMS software suite.

Positive-matrix factorization was applied to the time series of the organic component of the high-resolution mass spectra (Ulbrich et al., 2009). The present study focuses on one of the resolved statistical factors, referred to as the "IEPOX-SOA factor" (Hu et al., 2015). Diagnostics of the PMF analysis, especially as related to the resolved IEPOX-SOA factor, are presented in the Supplement (Section S2). A separate account is forthcoming to present the other PMF factors (de Sá, in preparation). Herein, factor profile and loading refer to the mathematical products of the multivariate statistical analysis, whereas mass spectrum and mass concentration refer to measurements.

In complement to the AMS data sets, mass concentrations of molecular and tracer organic species were measured using a Semi-Volatile Thermal Desorption Aerosol Gas Chromatograph (SV-TAG) at a time resolution of one hour. The instrument collected gas and particle samples, followed by thermal desorption, derivatization, and gas chromatography coupled to mass spectrometry (Isaacman et al., 2014). A summary of operational details for GoAmazon2014/5 is presented in the Supplement (Section S1), and the main account is presented in Isaacman-VanWertz et al. (2016).

Additional data sets used in the analysis were collected at the T3 site by instruments housed in the research container of the Mobile Aerosol Observing System (MAOS) of the ARM Climate Research Facility (ACRF) operated by the USA Department of Energy (Mather and Voyles, 2013; Martin et al., 2016c). A temperature-controlled inlet was mounted at 10 m above ground level. Measurements of nitrogen oxides were made using a chemiluminescence-based instrument (Air Quality Design). The measured odd-nitrogen family "NO_y", meaning NO_x +

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reservoir species, included NO, NO_2, HNO_3, organonitrates, particle nitrate, and peroxyacetyl nitrates. Further details of the NO_y measurements are presented in the Supplement (Section S1). Ozone concentrations were measured by an Ozone Analyzer (Thermo Fisher, model 49i). Particle number concentrations were measured by a Condensation Particle Counter (TSI, model 3772). Meteorological variables provided by the ARM Mobile Facility (AMF-1), which was also part of the ACRF, included wind direction, solar irradiance, and precipitation rate. Measurements of NO_y and particle number concentration onboard the G-1 aircraft of the ARM Aerial Facility (AAF) were also used in the analysis (Schmid et al., 2014; Martin et al., 2016c).

3. Results and Discussion

The organization of the presentation herein is as follows. The factor obtained from AMS PMF analysis is presented (Section 3.1), a case study comparing background to polluted conditions is discussed (Section 3.2), the roles of sulfate (Section 3.3) and nitric oxide (Section 3.4) in affecting factor loading are explored, and the influence of NO on production and loss processes of IEPOX-derived PM is considered (Section 3.5).

3.1 Statistical IEPOX-SOA factor

Positive-matrix factorization was carried out on the time series of AMS organic mass spectra. One statistical factor had a similar pattern of peak intensities as the "IEPOX-SOA factor" identified in other studies (Figure S1) (Robinson et al., 2011; Slowik et al., 2011; Budisulistiorini et al., 2013; Budisulistiorini et al., 2015; Chen et al., 2015; Xu et al., 2015). The Pearson correlation coefficient *R* between this factor and one obtained for a data set in the 2008 wet season in central Amazonia as part of the AMAZE-08 experiment was 0.99 (Chen et al., 2015). The ratio *f* of the factor loading to the mass concentration of submicron organic PM for the present study was 0.17 ± 0.09 (mean ± standard deviation). The IEPOX-SOA factor has been

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identified previously over the maritime tropical forest of Borneo (f = 0.23) (Robinson et al., 2011), in a rural area in Canada 70 km north of Toronto (f = 0.17) (Slowik et al., 2011), across several locations in the summertime southeastern USA (f = 0.17 to 0.41) (Budisulistiorini et al., 2013; Budisulistiorini et al., 2015; Hu et al., 2015; Xu et al., 2015; Budisulistiorini et al., 2016; Marais et al., 2016), and in AMAZE-08 (f = 0.34) (Chen et al., 2015).

The IEPOX-SOA factor reported herein had prominent peaks at m/z 53.04 and m/z 82.04 (Figure S1). The ion at m/z 82.04, corresponding to $C_5H_6O^+$, has been attributed to 3-methylfuran (3-MF). The thermal degradation of isoprene-derived PM upon mass spectral analysis was suggested as the source of 3-MF (Robinson et al., 2011). Lin et al. (2012) proposed that sequential dehydrations upon mass spectral analysis of 3-methyltetrahydrofuran-3,4-diols, which are an identified component of IEPOX-derived PM, can produce 3-MF. Other IEPOX-derived species as well as non-IEPOX species might also contribute to the production of $C_5H_6O^+$ ions (Surratt et al., 2010; Hu et al., 2015; Liu et al., 2016c).

Laboratory studies show that a mass spectrum having a pattern of peak intensities similar to that of the IEPOX-SOA factor is produced both by the uptake of IEPOX into aqueous acidic sulfate particles as well as by the photooxidation of isoprene under HO_2-dominant conditions in the presence of acidic sulfate particles (Budisulistiorini et al., 2013; Nguyen et al., 2014; Kuwata et al., 2015; Liu et al., 2015). The possibility of similar uptake by a broader range of liquid media remains to be fully tested, such as other acidic solutions as well as cloud waters. Compared to the laboratory spectra of (Liu et al., 2015), representing about 4 h of OH exposure at atmospheric concentrations (1.7×10^6 molec cm^{-3}), the main difference was the relative intensity of the m/z 44 peak. For the IEPOX-SOA factor of the present study, this peak was four times more intense

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(Figure S1), suggesting that the atmospheric PM was more oxidized. Hu et al. (2016) showed that heterogeneous aging of IEPOX-SOA can result in increased relative signal at *m/z* 44.

By contrast, laboratory studies show that a significantly different mass spectrum from that of the IEPOX-SOA factor is obtained for PM produced from isoprene photooxidation in the absence of aqueous particles (Krechmer et al., 2015; Kuwata et al., 2015). Under these conditions, chemical pathways other than IEPOX uptake into a liquid medium appear to be active, such as the condensation of low-volatility, multifunctional compounds produced by additional oxidation of ISOPOOH (Krechmer et al., 2015; Liu et al., 2016b; Riva et al., 2016b). This non-IEPOX pathway, however, is not expected to contribute a large fraction of the produced PM during the study period because of the high RH conditions in Amazonia and the prevalence of liquid particles for the prevailing atmospheric conditions (Bateman et al., 2016; de Sá, in preparation).

The SV-TAG measurements of the concentrations of C_5-alkene triols and 2-methyltetrols support the interpretation of the IEPOX-SOA factor as an indicator that PM was being produced, at least in significant part, from the reactive uptake of IEPOX (Claeys et al., 2004; Wang et al., 2005; Surratt et al., 2010). The factor loading strongly correlated with the concentrations of C_5-alkene triols (R = 0.96) and 2-methyltetrols (R = 0.78) (Figure 2). These species have been associated with the IEPOX reaction pathway in several laboratory studies (Surratt et al., 2010; Riedel et al., 2016). The R value with respect to C_5-alkene triols was independent of the f_{peak} value of the PMF solution, demonstrating the robustness of the relative time trend of factor loading even though the factor profile and absolute loadings changed across f_{peak} values (Figure S2d).

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The loading of the IEPOX-SOA factor may be an overestimate or an underestimate of the atmospheric concentration of the IEPOX-derived PM (Supplement, Section S2). The IEPOX-SOA factor can be understood as the net result of (i) produced IEPOX-derived PM, (ii) less that portion of the carbon that gets further oxidized and mixed into other PMF factors, and (iii) plus that portion of non-IEPOX-derived PM that gives rise to a similar AMS mass spectral pattern as the IEPOX-derived PM (Supplement, Section S2). Processes of type ii contribute to underestimates and processes of type iii lead to overestimates when using IEPOX-SOA factor loading as a surrogate for IEPOX-derived PM concentration. These uncertainties are qualitatively represented in Figure 1 by the brown dashed lines that enclose the fraction of particle material statistically captured by the factor analysis. The further analysis herein is based on using the loading of the IEPOX-SOA factor as a scalar proxy for the mass concentration of IEPOX-derived PM in a sampled air mass.

3.2 Background compared to polluted conditions

Under background conditions in the wet season, remote areas of the Amazon forest constitute one of the least polluted continental regions on Earth (Martin et al., 2010a). Nitric oxide (NO) concentrations characteristic of central Amazonia range from 20 to 70 ppt (Torres and Buchan, 1988; Bakwin et al., 1990; Levine et al., 2015). Daytime maximum ozone concentrations are 10 to 15 ppb (Rummel et al., 2007). Sulfate mass concentrations associated with in-basin processes are on average < 0.1 μg m^{-3}, and total background sulfate concentrations contributed by in- and out-of-basin processes rarely exceed 0.5 μg m^{-3} (Andreae et al., 1990; Chen et al., 2009).

In the wet season, Manaus emissions were the most important anthropogenic influence on observations at the T3 research site (Martin et al., 2016a). The afternoons of March 3 and 13,

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253 2014, are presented herein as representative cases of background and polluted conditions,
254 respectively. Both days were sunny, and major precipitation events were absent. Particle number
255 concentrations measured onboard the G-1 aircraft within the atmospheric boundary layer show
256 the position of the pollution plume on these two afternoons (Figure 3). NO_y concentrations
257 measured during the same flight are shown in Figure S3. The visualization in Figure 3 shows that
258 on March 3 the Manaus plume passed south of the T3 site. By comparison, on March 13 the
259 central portion of the plume passed over T3. Aircraft-based observations to track the Manaus
260 plume were available for 16 afternoons of the two-month study period. Ground site diagnostics
261 of the urban pollution reaching the T3 site were therefore also needed.

262 Measurements at ground level at the T3 site are plotted in Figure 4 for the afternoons of
263 March 3 (left panel) and March 13 (right panel). Based on wind speeds, the research site was 4 to
264 6 h downwind of Manaus (Martin et al., 2016c). Anthropogenic-biogenic interactions affecting
265 the production of IEPOX-derived PM were driven in large part by atmospheric photochemistry
266 at daybreak. Morning urban emissions followed by atmospheric processing arrived at the T3 site
267 during the local afternoon. The afternoon period, in addition to the connection to the Manaus
268 plume, was also characterized by reduced variability in other possible confounding variables,
269 such as temperature, radiation, and relative humidity. Figure 4 shows that on the afternoon of
270 March 3 ozone concentrations were below 10 ppb, particle number concentrations were below
271 1000 cm^{-3}, NO_y concentrations were less than 1 ppb, and sulfate concentrations were 0.3 to 0.4
272 µg m^{-3}. Species concentrations were stable throughout the afternoon. On March 13, ozone
273 concentrations exceeded 30 ppb for most of the afternoon, particle concentrations reached 10,000
274 cm^{-3}, NO_y concentrations consistently exceeded 1 ppb, and sulfate concentrations were 0.3 to 0.6

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275 µg m^{-3}. Concentrations fluctuated markedly throughout the afternoon on March 13, reflecting
276 different levels of pollution influence in the air passing over the T3 site during that period.
277 Elevated concentrations of ozone, particle number, and NO_y were reliable markers of
278 pollution influence over the course of the study period (Supplement, Section S3). Pollution was
279 associated with stronger relative enhancements in NO_y concentrations than in sulfate
280 concentrations (Sections 3.3 and 3.4). With respect to the IEPOX-SOA factor, Figure 4 shows
281 that the absolute and relative loadings decreased for the polluted compared to background
282 conditions. Relative loadings are expressed by the ratio *f* of IEPOX-SOA factor loading to the
283 organic PM mass concentration. Decreased absolute and relative factor loadings under polluted
284 conditions, presented in Figure 4 as a case study, also characterized the data sets of the entire
285 study period. Other examples are presented in the Supplement (Figure S4).

286 **3.3 Sulfate as a driver of IEPOX-derived PM production**

287 A scatter plot between sulfate mass concentrations and IEPOX-SOA factor loadings for
288 all afternoon periods is shown in Figure 5a. Background and polluted conditions are represented
289 in the data set. For further visualization, the data set was organized into six subsets based on
290 sulfate concentration. The medians and the means of the subsets are plotted in the figure. The
291 visualization shows that sulfate concentration served as a first-order predictor of the IEPOX-
292 SOA factor loading in central Amazonia in the wet season. The explanation can be a
293 combination of increased acidity, greater reaction volume including by enhanced hygroscopic
294 growth, and possibly a nucleophilic role for sulfate (Xu et al., 2015; Marais et al., 2016). An
295 analysis of the relative importance of each is out of the scope of the present study (Supplement,
296 Section S4).

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297 For Figure 5a, the coefficient R^2 of determination between sulfate mass concentration and
298 factor loading was 0.37, meaning that 37% of the variance of the IEPOX-SOA factor loading
299 was explained by sulfate mass concentration. As a point of comparison, R^2 varied between 0.4
300 and 0.6 for observations in the southeastern USA, which seasonally is a region of high isoprene
301 emissions (Budisulistiorini et al., 2013; Budisulistiorini et al., 2015; Hu et al., 2015; Xu et al.,
302 2015). A chemical transport model that predicted IEPOX-derived PM mass concentrations for
303 the southeastern USA obtained R^2 of 0.4 for the relationship to predicted sulfate mass
304 concentration (Marais et al., 2016). The model attributed the correlation to the acidity and
305 particle volume provided by sulfate, both of which favored IEPOX uptake. Central Amazonia
306 and the southeastern USA differ considerably in terms of meteorology, chemistry, and levels of
307 regional pollution, yet they have in common an important role of sulfate concentration as a
308 predictor of IEPOX-derived PM concentration, even as the sulfate concentrations themselves
309 differ by an order of magnitude. Sulfate concentrations typically had an interquartile range of
310 [1.5, 3.0] μg m^{-3} in the studies in the southeastern USA, which can be compared to a range of
311 [0.11, 0.36] μg m^{-3} under background conditions during the wet season in central Amazonia.
312 A key difference between the southeastern USA and central Amazonia is the role of
313 sulfate concentration as a clear or ambiguous indicator, respectively, of urban influence. For the
314 relatively low sulfate mass concentrations (<0.5 μg m^{-3}) characteristic of the study period,
315 background air in central Amazonia contributed significantly to the variability in sulfate
316 concentration measured at the T3 site. Background concentrations of sulfate in Amazonia,
317 distinguished from sulfate tied to the urban Manaus plume, originated from in-basin emissions of
318 dimethyl sulfide (DMS) and hydrogen sulfide (H_2S) from the forest as well as from out-of-basin
319 marine emissions from the Atlantic Ocean (Andreae et al., 1990; Chen et al., 2009; Martin et al.,

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2010a). In the wet season, biomass burning from Africa and to a lesser extent from South America also episodically contributed significantly to sulfate concentrations in the Manaus region. In addition, emissions from large cities on the eastern coast of Brazil were important at times when rare meteorological events shifted the northeasterlies typical of the wet season to easterlies (Martin et al., 2016a). Manaus contributions to sulfate mass concentrations in an air mass were in addition to these various background sources.

The relative importance of Manaus contributions to the sulfate concentrations in the air masses that passed over T3 was assessed by comparison of the probability density function of sulfate concentration at T3 to those of sites upwind of Manaus (Figure 5b). The distributions of the two upwind sites had a central tendency of 0.05 to 0.3 μg m^{-3}, suggesting the range of natural concentrations, and a rightside skewness up to 0.6 μg m^{-3}, suggesting the importance of episodic long-range transport (Chen et al., 2009). The figure shows that the distribution at T3 did not differ greatly from those of the upwind sites even though the air masses over T3 regularly transported Manaus pollution, indicating that Manaus did not constitute a dominant sulfate source in the region. Elevated sulfate concentrations on any one afternoon at the T3 site might have arisen because of elevated background concentrations on that day rather than the influence of the Manaus pollution plume. The implications are that (i) sulfate concentration was an ambiguous indicator of urban influence at the T3 site and (ii) increases in sulfate concentrations in pollution events were moderate relative to background concentrations.

3.4 NO as a modulator of IEPOX-derived PM production

In the transport from Manaus to the T3 research site, NO concentration is not conserved, in part because of reactions with ozone and organic peroxy radicals(Martin et al., 2016a). In this case, the instantaneous NO concentrations measured at the T3 site do not directly provide

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information about the fate of ISOPOO radicals along the transport time of 4 to 6 h from Manaus to the T3 site. The collective contributions of NO, NO_2, and their oxidation products are, however, reflected in measurements of NO_y concentrations at the T3 site. The NO_y family is expected to have a longer lifetime than the transport time from Manaus to the T3 site (Romer et al., 2016). The NO_y concentration measured at T3 therefore served as a surrogate for the integrated exposure of the airmass to NO chemistry between Manaus and T3 (Liu et al., 2016a).

Unlike the ambiguity associated with the sulfate concentration, an elevated NO_y concentration served as a clear indicator of anthropogenic influence in an air mass passing over the T3 site. For background conditions over the forest, NO_y originated from NO emitted from soils and other natural sources such as lightning (Bakwin et al., 1990; Jacob and Wofsy, 1990). The probability density function of NO_y concentration under background conditions in the wet season of the central Amazon basin is shown in Figure 6b (Bakwin et al., 1990). The distribution for measurements at T3 is also shown. Relative to the narrow distribution around 0.5 ppb for background conditions, there is high-side skewness extending up to 4 ppb for the T3 measurements, indicating the clear influence of Manaus emissions on NO_y concentrations.

NO_y concentration was incorporated into the analysis by segregation of the dataset of Figure 5a into five subsets (Supplement, Section S5). Linear fits to the NO_y-segregated data subsets are plotted in Figure 6a. Each subset is represented by a different color. Parameter values of the associated fits are listed in Table 1. In conjunction with sulfate concentration, the visualization presented in Figure 6a shows that NO_y concentration further explained the variability in IEPOX-SOA factor loadings. The R^2 values, representing the extent to which sulfate was able to explain variability in IEPOX-SOA factor loading once isolated for NO_y concentration, were higher for the data subsets having lower and higher extremes of NO_y

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366 concentrations (Table 1). These conditions represent the limiting cases of fully background
367 conditions for the former and the strongest effects of Manaus pollution for the latter. By
368 comparison, intermediate NO_y concentrations could arise from air masses that mixed together
369 background air with Manaus pollution during the transport to T3 (e.g., by entrainment) and thus
370 represent complex processing. Single or multiple mixing points could occur anywhere along the
371 path from Manaus to T3, thus introducing variability into the effective photochemical age of the
372 air mass arriving at T3 and resulting in lower R^2 values for intermediate NO_y concentrations. In
373 caveat, this explanation assumes that NO emissions from Manaus had low day-to-day variability.
374 In relation to the influence of Manaus pollution, sulfate concentration was affected by a
375 mixture of background and urban sources whereas NO_y concentration largely had urban sources.
376 As an approximation to keeping the sulfate concentration constant and thus focusing on the role
377 of NO in the urban pollution, the visualization of the dependence of IEPOX-SOA factor loading
378 on NO_y concentration was further refined by taking data subsets segregated by low (< 0.1 μg
379 m^{-3}) and high (> 0.3 μg m^{-3}) sulfate concentrations. Figures 7a, 7b, and 7c show the factor
380 loading, organic PM mass concentration, and the ratio *f* of the IEPOX-SOA factor loading to the
381 organic PM mass concentration, respectively, plotted against NO_y concentration for low and high
382 sulfate concentrations.
383 Figure 7a shows that for both low and high sulfate concentrations an increase in NO_y
384 concentration from background to polluted concentrations was associated with a decrease in the
385 IEPOX-SOA factor loading by two to three times. For low sulfate concentration, the interquartile
386 range of the factor loading decreased from [0.037, 0.093] to [0.022, 0.039] μg m^{-3} for an increase
387 in NO_y concentration from 0.5 to 2 pbb. For high sulfate concentration, the factor loading
388 decreased from [0.57, 0.95] to [0.21, 0.35] μg m^{-3} for the same transition in NO_y concentration.

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The greatest changes in factor loading were in the region of 1 ppb NO_y. This region of greatest sensitivity coincided with the transition from background to polluted conditions. For the same time period, a change was reported in the gas phase from a dominance of ISOPOOH to MVK/MACR products across this transition in NO_y concentration (Liu et al., 2016a).

Figure 7b shows that for both low and high sulfate concentrations the organic PM mass concentration M_{org} and the IEPOX-SOA factor loading had opposite trends for low compared to intermediate NO_y concentrations, even though the trend in M_{org} was less steep. The factor loadings decreased by 60% whereas the M_{org} increased by 25% for 0.5 to 2 ppb NO_y (Figures 7a and 7b). Increases in M_{org} can include contributions from secondary PM produced by enhanced concentrations of hydroxyl radicals and ozone in the pollution plume as well as from primary PM emitted from the Manaus urban region (Martin et al., 2016a; de Sá, in preparation). For higher NO_y concentrations (> 2 ppb), however, Figure 7b shows that M_{org} decreased after a peak value, approaching values close to background under the most polluted conditions. The chemistry can become sufficiently shifted that more-volatile gas-phase products can be produced (Pandis et al., 1991; Kroll et al., 2005; Carlton et al., 2009). In addition, hydroxyl radical concentrations can also decrease because of titration by NO_2 (Valin et al., 2013; Rohrer et al., 2014). An increase in total organic mass concentration could possibly contribute to a decrease in IEPOX-derived PM production by kinetically limiting the uptake of IEPOX (Gaston et al., 2014; Lin et al., 2014; Riva et al., 2016a). The dominant effect of the urban plume, however, seems to be that of shifting the fate of ISOPOO radicals through the increase in NO, thereby significantly decreasing the production of ISOPOOH (Liu et al., 2016a) (Section 3.5).

The combined trends of Figures 7a and 7b for increasing NO_y are represented in Figure 7c as the ratio *f*. The figure shows that *f* decreased for increasing NO_y concentration for both low

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412 and high sulfate concentrations. The greatest decrease occurred across the range of NO_y
413 concentrations that represented the shift from background to polluted conditions. For low sulfate
414 concentration, the interquartile range of *f* decreased from [0.09, 0.18] to [0.04, 0.09] for an
415 increase in NO_y concentration from 0.5 to 2 ppb. These ranges shifted to [0.35, 0.40] and [0.07,
416 0.18] for high sulfate concentration. The magnitude of the decrease for high sulfate
417 concentrations suggests that IEPOX-derived PM shifted from being a major to a minor
418 component of the PM, although the caveats related to under- and overestimates connected to the
419 IEPOX-SOA factor should be kept in mind (vide supra). Taken together, the results shown in
420 Figure 7 demonstrate how urban pollution affected the production and composition of regional
421 IEPOX-derived PM.

422 The data sets presented in Figures 5, 6, and 7 lead to the conclusion that the additional
423 NO concentrations contributed by Manaus emissions typically suppress the production of
424 IEPOX-derived PM to a greater extent than the additional sulfate concentrations enhance it.
425 Figure 8 presents a systematic visualization. The factor loadings at T3 are represented as
426 contours for axes of sulfate and NO_y concentrations. Higher factor loadings are favored for
427 higher sulfate and lower NO_y concentrations. Factor loadings are most sensitive to changing
428 concentration in the high-sulfate, low-NO_y region. The gray dashed line in Figure 8 represents a
429 qualitative divisor between domains of typical background and polluted conditions downwind of
430 Manaus.

431 **3.5 Influence of NO on production and loss processes of IEPOX-derived PM**

432 Elevated NO may affect both the production and loss processes of IEPOX-derived PM.
433 On the one hand, production may be reduced because of increased scavenging of ISOPOO by
434 NO, thus obviating production of IEPOX and consequently of IEPOX-derived PM. Production

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435 may also be reduced because of more rapid gas-phase loss of IEPOX in response to elevated OH
436 and O_3 concentrations. On the other hand, loss of IEPOX-derived PM may be enhanced due to
437 faster processing of its characteristic compounds by the elevated oxidant concentrations.

438 A Lagrangian model is employed to help delineate the relative importance of reduced
439 production compared to enhanced loss on the observed IEPOX-derived PM concentrations. The
440 model is initialized by background air that passes over Manaus in the mid-morning. The
441 evolution of IEPOX-derived PM in that air mass is modeled under either polluted or background
442 conditions for arrival at the T3 site in the afternoon. The governing differential equation of the
443 model represents the sum of production and loss processes affecting the concentrations of
444 IEPOX-derived PM, as follows:

445 $$\frac{dM}{dt} = -\alpha_L k_L M + \alpha_P k_P \quad (1)$$

446 where M designates the IEPOX-derived PM mass concentration, t designates time, and the first
447 and second terms on the right-hand side represent loss and production processes, respectively.
448 Table 2 lists other symbol definitions and units.

449 The analytic solution of Equation 1 for time t is presented in the Supplement (Section
450 S6). From this solution, characteristic times τ for production and loss processes for polluted
451 compared to background conditions are as follows: $\tau_{P,pol} = M_0 / (\alpha_P k_P)$, $\tau_{P,bg} = M_0 / k_P$, $\tau_{L,pol} = 1 /$
452 $(\alpha_L k_L)$, and $\tau_{L,bg} = 1 / k_L$ (Supplement, Section S6). The term M_0 represents the IEPOX-derived
453 PM mass concentration just upwind of Manaus. Under background conditions, the enhancement
454 factors α_L and α_P are unity by definition. Under polluted conditions, $\alpha_L = 2$ and $\alpha_P = 0.1$ to reflect
455 enhanced loss and decreased production, respectively. Further descriptions of the model and
456 assumptions are presented in the Supplement (Section S6).

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The analysis strategy is to compare τ_P and τ_L to the transport time τ_{tr} under polluted and background conditions to assess the relative importance of altered production and loss processes for IEPOX-derived PM from Manaus to T3. The mode value for τ_{tr} is 4 h based on trajectory analysis (Martin et al., 2016c). Intervals for the characteristic times τ_P and τ_L are constrained by the T3 afternoon data sets. Concentration ratios ξ, defined as $\xi = M_{pol} / M_{bg}$, are used to constrain the model (Table 3). The quantities M_{pol} and M_{bg} denote $M(t = \tau_{tr})$, meaning the mass concentration at T3 under polluted or background conditions, respectively. The use of the ratio quantity ξ in the analysis, rather than absolute concentrations, provides increased robustness because of low variability in ξ across the observed range of sulfate concentrations, even as M_{pol} and M_{bg} vary greatly (Table 3). The possible impact of over- or underestimates of IEPOX-derived PM mass concentration, as a consequence of using IEPOX-SOA factor loading as a surrogate, is also mitigated by the use of ξ.

Two cases of the model (1 and 2) are presented, respectively focusing on constraining k_P or k_L and consequently τ_P or τ_L (Table 4). The results for Case 1 of the analysis are shown in Figure 9a. The value of k_P is varied from 0 to 0.2 μg m^{-3} h^{-1} while the other model parameters are held constant. The loss rate coefficient k_L is fixed at 0.015 h^{-1}, corresponding to a characteristic time of 2.8 days (Supplement, Section S6). Based on observed values of ξ (gray shaded area in Figure 9a), an interval for k_P of [0.07, 0.13] μg m^{-3} h^{-1} is obtained, as indicated by the vertical dashed lines. Across this interval, M_{bg} and M_{pol} vary from 0.49 to 0.72 μg m^{-3} and 0.23 to 0.25 μg m^{-3}, respectively, which are consistent with the observed IEPOX-SOA factor loadings (Table 3). The modeled production times have intervals of [1.8, 3.3] h for $\tau_{P,bg}$ and [18, 33] h for $\tau_{P,pol}$.

Case 2 of the analysis evaluates constraints on the loss rate coefficient k_L, and results are shown in Figure 9b. Loss processes can include chemistry, such as heterogeneous oxidation or

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other in-particle reactions that reduce the IEPOX-SOA factor loading, as well as physical mechanisms, such as particle deposition and particle dilution by entrainment that reduce mass concentrations of IEPOX-derived PM (Supplement, Section S6). The value of k_L is varied over three orders of magnitude, representing characteristic times of hours to weeks, while the other model parameters are held constant (Table 4). The production rate coefficient k_P is fixed at 0.10 μg m^{-3} h^{-1}, corresponding to the interval midpoint of Case 1. The observed values of ξ (gray shaded area) in intersection with the modeled values of ξ imply an upper limit on k_L at 0.043 h^{-1}, corresponding to characteristic times of a day to weeks (Figure 9b). Correspondingly, $\tau_{L,bg,}$ > 24 h under background conditions, and $\tau_{L,pol}$ > 12 h under polluted conditions.

The analyses of Cases 1 and 2 constrain the values of $\tau_{P,pol}$, $\tau_{P,bg}$, $\tau_{L,pol}$, and $\tau_{L,bg}$ based on the observed values of ξ. The lower limits of the characteristic times for loss, meaning $\tau_{L,bg,}$ > 24 h and $\tau_{L,pol}$ > 12 h, are considerably longer than the transport time of 4 h under both background and polluted conditions. Enhanced loss, therefore, does not explain alone the observed values of ξ. By comparison, the observed values of ξ imply a shift in the characteristic time for production from [1.8, 3.3] h under background conditions to [18, 33] h under pollution conditions. The shift in timescale is significant in light of the transport time of 4 h. Therefore, reduced production, rather than enhanced loss, is consistent with the lower IEPOX-derived PM concentrations under polluted conditions. A few afternoon hours of altered isoprene chemistry is sufficient to significantly shift the atmospheric concentration of IEPOX-derived PM.

4. Summary and conclusions

The influence of anthropogenic emissions on the production of organic particulate matter from isoprene epoxydiols was studied during the wet season of the tropical forest in central Amazonia. The IEPOX-derived PM concentration at the T3 site, as indicated by the IEPOX-

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503 SOA factor loading, was lower under polluted compared to background conditions. Sulfate
504 concentration was an important first-order predictor of the IEPOX-SOA factor loading,
505 corroborating the understanding of the role of sulfate in the production of IEPOX-derived PM
506 that has been developed in laboratory studies as well as in investigations in the southeastern USA
507 (Surratt et al., 2007b; Budisulistiorini et al., 2013; Budisulistiorini et al., 2015; Hu et al., 2015;
508 Kuwata et al., 2015; Xu et al., 2015). Unlike the southeastern USA, however, where
509 anthropogenic influences dominated variability in sulfate concentrations, contributions by the
510 Manaus urban region to sulfate concentrations were of approximately equal magnitude to the
511 background variability in central Amazonia. By comparison, Manaus urban emissions of NO
512 dominated over background concentrations, and the NO_y concentration measured 4 to 6 h
513 downwind of Manaus at the T3 site was an important predictor of the IEPOX-SOA factor
514 loading. In net effect, the suppression of IEPOX production because of elevated NO
515 concentrations in the pollution plume dominated over any enhancements in IEPOX uptake
516 because of greater sulfate concentrations.

517 The dependence of the IEPOX-SOA factor loadings on both sulfate and NO_y
518 concentrations, as shown in Figure 8, suggests that altered net anthropogenic effects may be
519 expected for different geographic regions, even within Amazonia, and different time periods,
520 such as the wet and dry seasons. The T3 site experienced a wide range of NO_y concentrations,
521 allowing for the systematic demonstration of the dependence of IEPOX-derived PM
522 concentrations on NO_y concentrations. The results show that the transition in isoprene
523 photochemistry related to the production of IEPOX-derived PM is most sensitive precisely at the
524 transition between background and polluted conditions, around 1 ppb of NO_y, at least for central
525 Amazonia in the wet season. These findings suggest that the fraction of PM derived from IEPOX

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might be lower and have lower variability for other geographic regions characterized by higher NO_y baseline concentrations (e.g., upward of 1 to 2 ppb). For regions further downwind of the urban center, the effects of the plume are expected to phase out both due to dilution and to consumption of NO, and a gradual transition to background chemistry is expected to take place. Adequately representing background conditions and the transition to polluted conditions within models, including the dependence of the production of IEPOX-derived PM not only on sulfate but also on NO concentration, is thus important for making accurate predictions of PM concentrations, both in Amazonia and around the globe.

The findings herein can be considered in the context of Amazonia in transition (Davidson et al., 2012). In the past 50 years, the metropolitan area of Manaus, today at more than 2 million inhabitants, has experienced rapid economic and population growth (Martin et al., 2016c). Changes in the fuel matrix, such as the ongoing shift from high-sulfur to low-sulfur oil in the vehicle fleet as well as from fuel oil to natural gas in many power plants (Medeiros et al., in preparation), are changing the composition of the Manaus pollution plume. Based on the findings presented herein, a reduction in sulfate sources from Manaus would not be expected to considerably affect the mass concentration of IEPOX-derived species in forest regions affected by the plume. Background sources independent of Manaus appear sufficient to sustain sulfate concentrations regionally. On the other hand, in the absence of pollution control technologies, NO emissions can be expected to increase in coming years due to the development of more efficient (i.e., higher temperature) sources of electricity associated with the development of natural gas resources in the basin, as well as from growth in transportation associated with increased population. Increased NO concentrations can be expected to reduce the mass concentration of IEPOX-derived species in forest regions affected by the plume. Changes in the

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549 atmospheric particle population can have follow-on effects on cloud type, duration, and rainfall
550 (Pöschl et al., 2010). In addition to PM derived from IEPOX as discussed herein, a better
551 understanding of other pathways that also contribute to organic PM, as well as possible changes
552 to those pathways with increasing pollution in the region, warrants further study so as to achieve
553 sufficient knowledge for decision-making related to air quality and climate in Amazonia.

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Group	NO_y range (ppb)	Fit slope	Fit intercept	Fit R^2
1	< 0.66	2.16	-0.13	0.75
2	0.66 – 0.92	1.48	-0.04	0.64
3	0.92 – 1.55	0.78	0.06	0.24
4	1.55 – 2.45	0.71	-0.01	0.44
5	> 2.45	0.55	-0.02	0.62

Table 1. Parameters associated with NO_y groupings in Figure 6. Listed are the NO_y concentrations and the parameters for least-squares linear fits to each group. R^2 represents the coefficient of determination.

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Symbol	Description	Unit
M	mass concentration of IEPOX-derived PM	μg m^{-3}
t	time	h
k_P	zero-order rate coefficient for production under background conditions	μg m^{-3} h^{-1}
k_L	first-order rate coefficient for loss under background conditions	h^{-1}
α	multiplicative factor representing the effects of Manaus pollution on rate coefficients	
τ	characteristic time of a process (e.g., production, loss, or transport)	h
Subscript *tr*	Refers to transport	
Subscript *bg*	Refers to background conditions	
Subscript *pol*	Refers to polluted conditions	
Subscript 0	Refers to an initial state (i.e., just upwind of Manaus)	
Subscript *P*	Refers to production processes	
Subscript *L*	Refers to loss processes	

Table 2. Descriptions and units of symbols in the model.

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	Loading (μg m^{-3}) for background conditions		Loading (μg m^{-3}) for polluted conditions		Ratio ξ	
	Low sulfate	High sulfate	Low sulfate	High sulfate	Low sulfate	High sulfate
IEPOX-SOA factor	[0.037, 0.093]	[0.57, 0.95]	[0.022, 0.039]	[0.21, 0.35]	0.47	0.35

Table 3. Interquartile intervals of IEPOX-SOA factor loadings observed for background and polluted conditions. Background and polluted conditions correspond to approximately 0.5 ppb and 2 ppb of NO_y, respectively. The table also lists the resulting ratio ξ of the median factor loading under polluted compared to background conditions.

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Model case	Parameter values				Initial condition
	k_P	k_L	α_P	α_L	M_0
1. Vary k_P	0 to 0.2	0.018	0.1	3	0.23
2. Vary k_L	0.065	0.001 to 1	0.1	3	0.23

Table 4. Parameter values and initial conditions used in model cases. Descriptions and units are listed in Table 2. The M_0 value is based on the mean IEPOX-SOA factor loading that was measured from 14:00-16:00 UTC (10:00-12:00 local time) at a regional background site during two months of the wet season in 2008 (Chen et al., 2015). For comparison, a similar value of 0.19 μg m^{-3} was obtained during the present study as the mean value observed at the T3 site for NO_y < 1 ppb (14:00-16:00 UTC).

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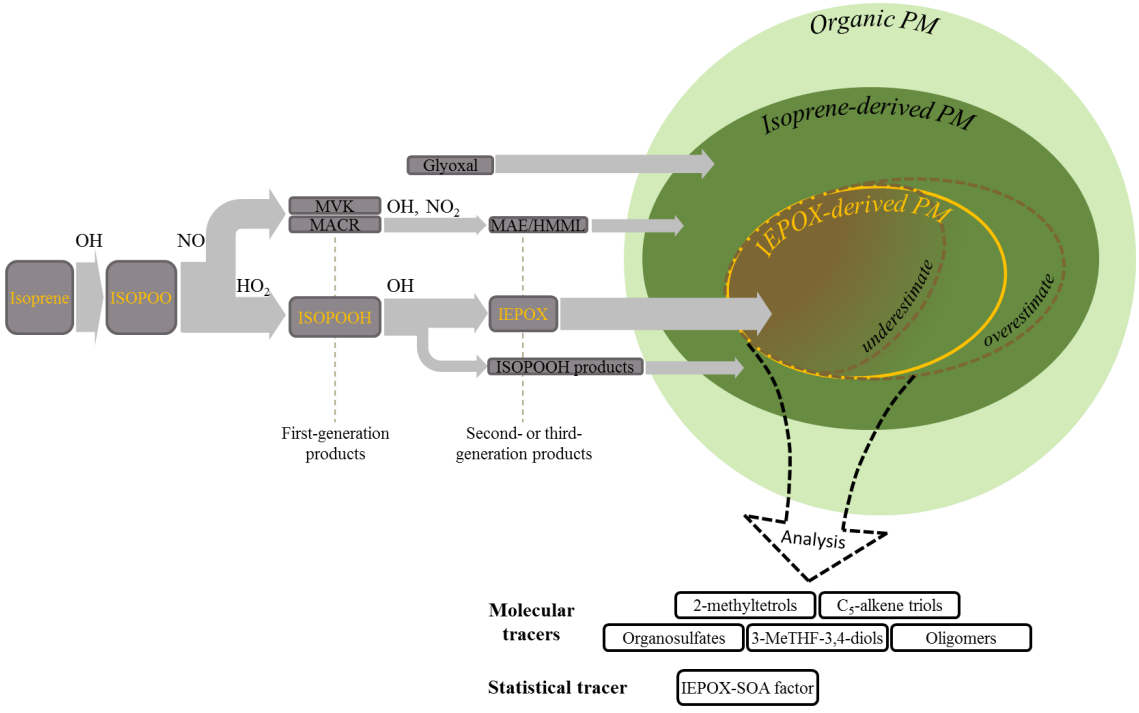

Figure 1. Schematic diagram for the production of IEPOX-derived PM from the photooxidation of isoprene. Organic peroxy radicals (ISOPOO), produced by OH attack and O_2 addition to isoprene, are scavenged along NO or HO_2 pathways. By the HO_2 pathway, organic hydroperoxides (ISOPOOH) are first-generation products that react with additional OH to produce isoprene epoxydiols (IEPOX). The IEPOX species undergo reactive uptake into particles, ultimately producing IEPOX-derived particulate matter. Arrow thickness qualitatively illustrates the relative importance (i.e., mass flux) of a reaction channel under background conditions. Gray and green background colors indicate species in the gas and particle phases, respectively. The light-green disk represents the total organic PM. Within that disk, the contribution by isoprene-derived PM, including compounds produced both IEPOX and non-IEPOX pathways, is represented by the dark-green oval. Inside that oval, the contribution by IEPOX-derived PM is represented by the yellow oval region. The color gradient between brown and dark green illustrates the chemical modification of the IEPOX-derived PM over time. The large dashed black arrow represents the analytical methods that use different types of molecular and statistical tracers (listed in the boxes) to quantify the IEPOX-derived PM mass concentrations. For simplicity, the figure omits the many routes leading to the production of glyoxal (Fu et al., 2008), possible ISOPOO isomerization when NO and HO_2 concentrations are sufficiently low (Crounse et al., 2011; Liu et al., 2016a), second-generation production of peroxymethylacrylic nitric anhydride (Lin et al., 2013; Nguyen et al., 2015), and particle water and other inorganic components. 3-methyltetrahydrofuran-3,4-diols are abbreviated as 3-MeTHF-3,4-diols. Other abbreviations are provided in the main text.

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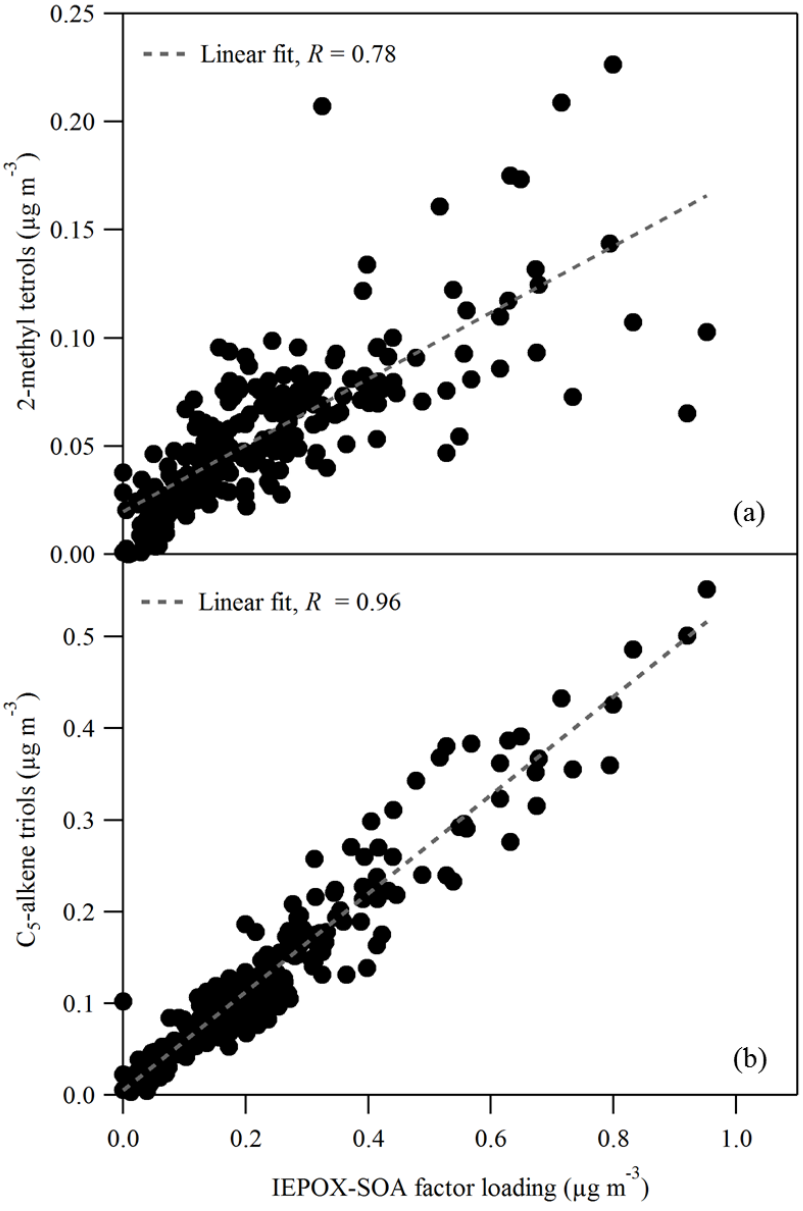

Figure 2. Scatter plot of the loading of the IEPOX-SOA factor derived from analysis of the AMS data set and the mass concentrations of C_5-alkene triols and 2-methyltetrols measured by SV-TAG. All data collected during IOP1 are included, meaning that the plotted data are not limited to afternoon time periods.

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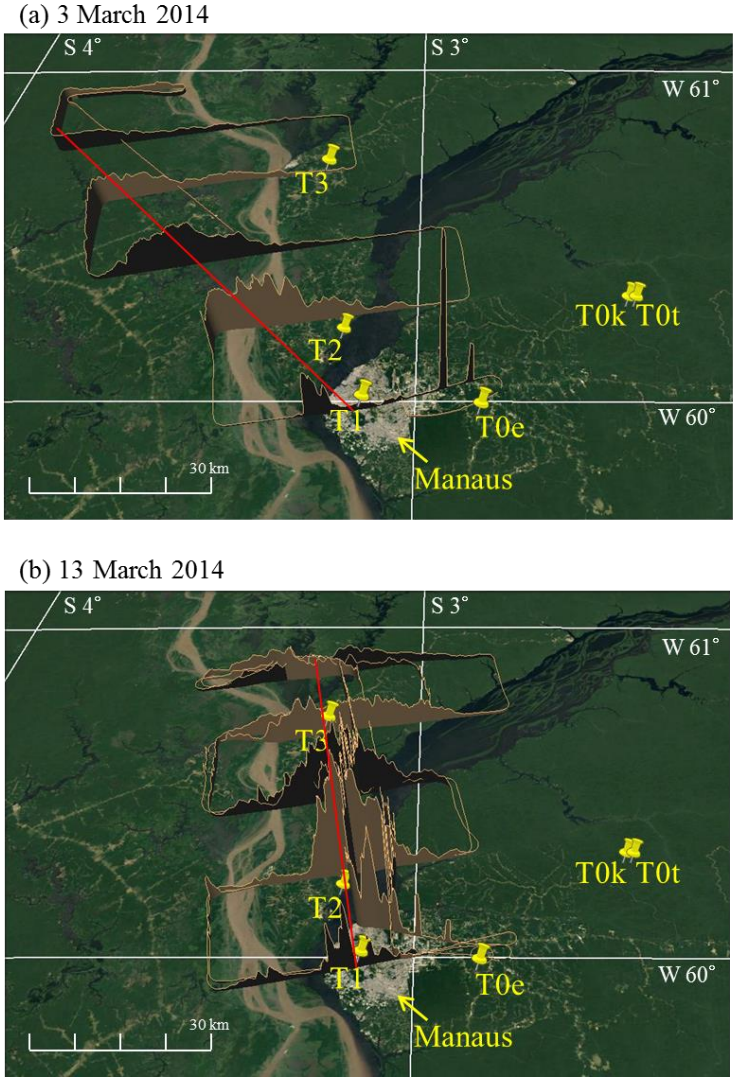

Figure 3. Visualization of the Manaus pollution plume by plotting particle number concentrations in the vertical axis. Observations took place on flights from late morning to early afternoon on (a) March 3, 2014, 17:45 – 19:26 UTC, and (b) March 13, 2014, 14:14 – 17:21 UTC. Local time is UTC minus 4 h. The red lines guide the eye through the central axis of the plume. The direction and extent of the plume was observed by the G-1 aircraft within the atmospheric boundary layer downwind of Manaus. Measured particle number concentrations are plotted on a vertical axis on top of an image of land cover in the horizontal plane. Particle concentrations in the center of the plume ranged from 10,000 to 25,000 cm^{-3} nearby Manaus. Yellow pins indicate the locations of some of the GoAmazon2014/5 research sites, including T3 (Martin et al., 2016c).

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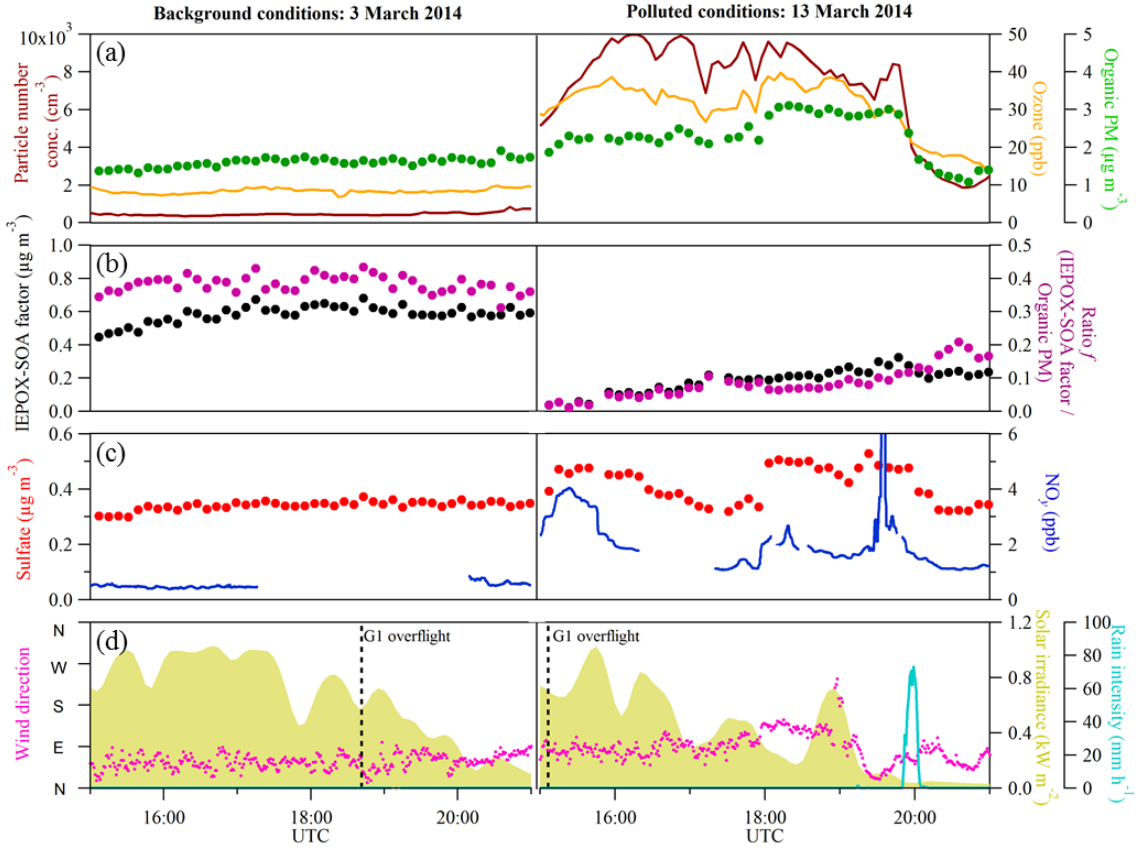

Figure 4. Case studies of (left) background and (right) polluted air masses passing over T3 on afternoons of March 3 and 13, 2014. (a) Ozone, particle number, and organic mass concentration. (b) IEPOX-SOA factor loading and the ratio *f* of the factor loading to the organic PM concentration. (c) Sulfate and NO_y concentrations. (d) Wind direction, rain intensity, and solar irradiance. Local time is UTC minus 4 h. Time points of overflights at 500 m by the G-1 research aircraft are marked by the dashed line (Martin et al., 2016a).

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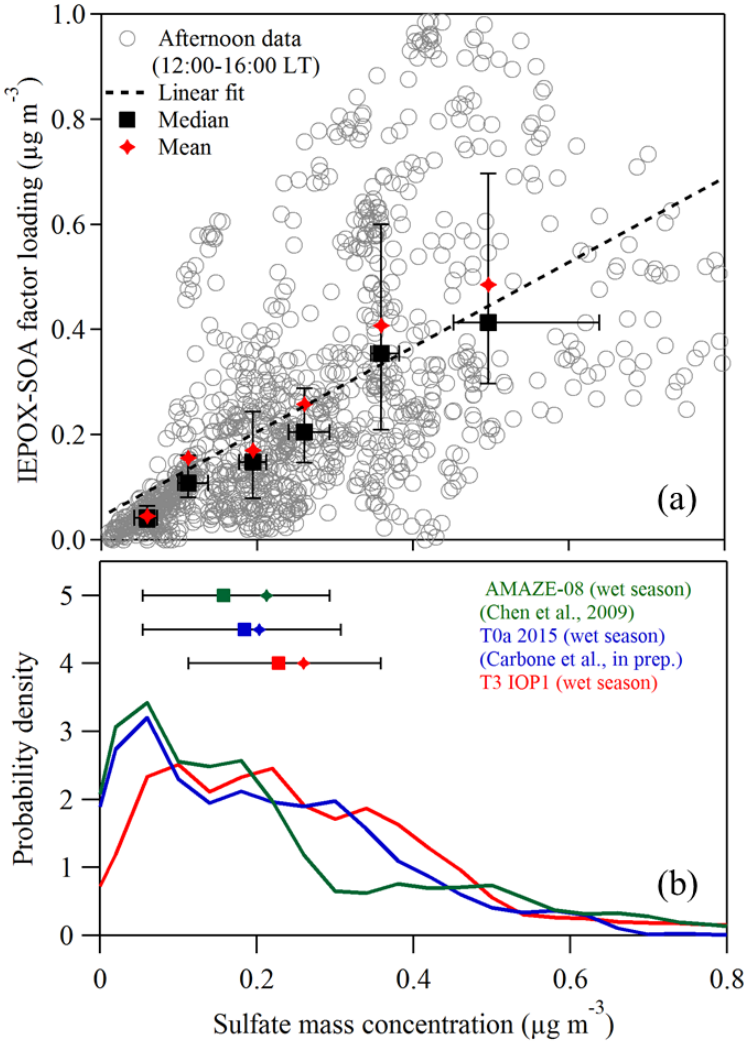

Figure 5. (a) Scatter plot of sulfate mass concentration and IEPOX-SOA factor loading. A least-squares linear fit is represented by the dashed line (R^2 = 0.37). The data set was collected into six subsets based on sulfate concentration to calculate statistics. Medians (squares) and means (diamonds) of each subset are plotted. Whiskers on the medians represent the interquartile ranges. (b) Probability density function of sulfate mass concentration at the background site T0t ("TT34") north of Manaus in the wet season of 2008 (Chen et al., 2009; Martin et al., 2010b; Martin et al., 2016b), at the background site T0a ("ATTO") northeast of Manaus in the wet season of 2015 (Andreae et al., 2015), and at T3 during the wet season of 2014 (IOP1). The plotted data sets were recorded during local afternoons (12:00-16:00 local time; 16:00-20:00 UTC). Means (diamonds), medians (squares), and interquartile range (whiskers) are shown for the probability density functions.

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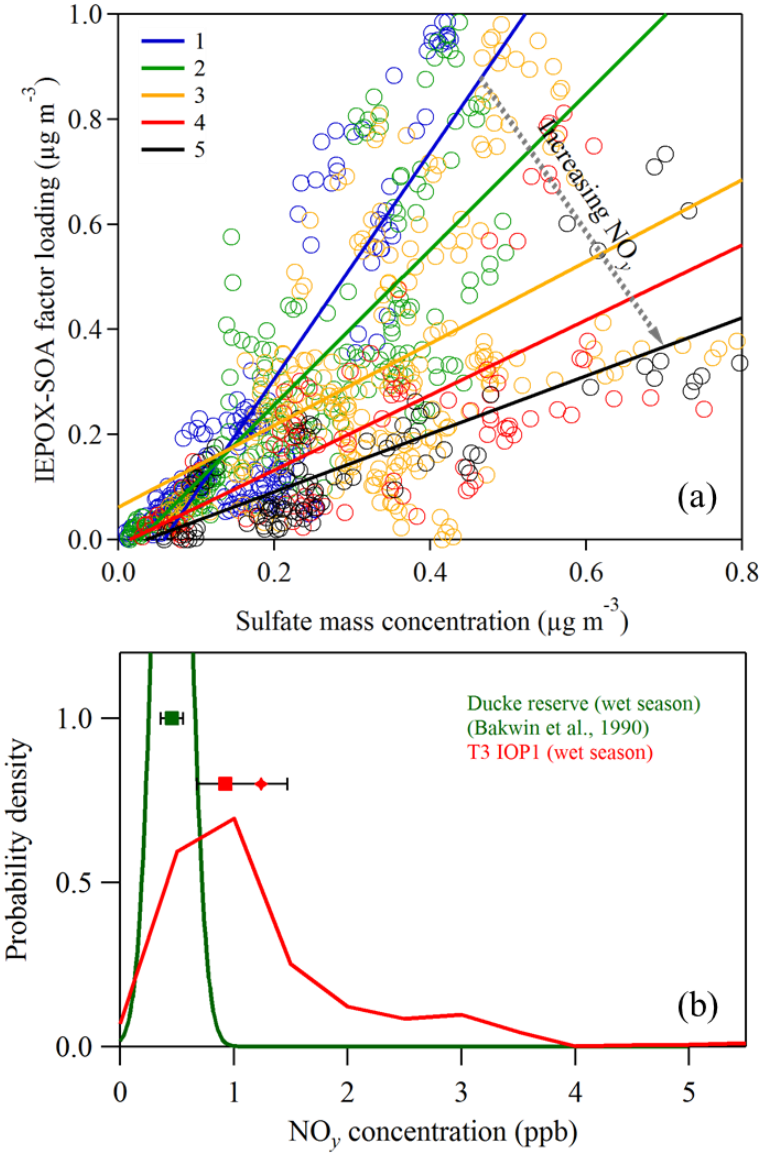

Figure 6. (a) Scatter plot of sulfate mass concentration and IEPOX-SOA factor loading for local afternoon (12:00-16:00 local time; 16:00-20:00 UTC). The data sets were collected into five subsets, colored and labeled 1 to 5, based on NO_y concentration. Table 1 presents the parameters of the five least-squares linear fits represented by the colored lines in the figure. (b) Probability density function of NO_y concentration at a background site nearby Manaus in the wet season of 1987 (Bakwin et al., 1990) and at T3 during the wet season of 2014 (IOP1) (afternoon data). Means (diamonds), medians (squares), and interquartile range (whiskers) are shown for the probability density functions. Additional analysis of panel (a) is discussed in the Supplement (Section S5) related to Figure S5.

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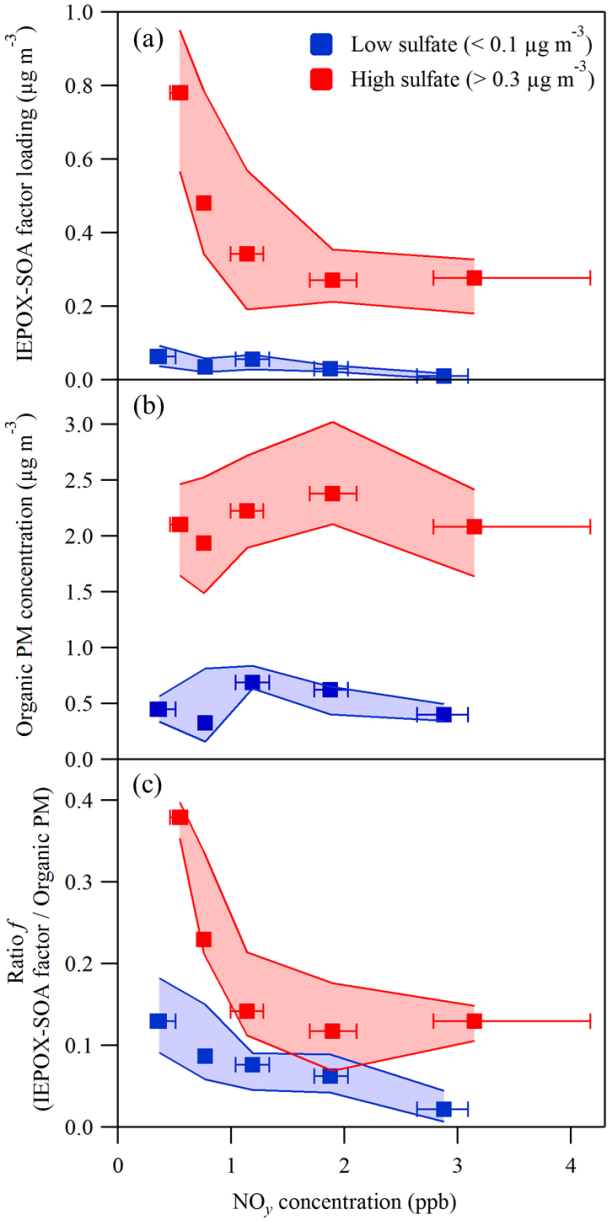

Figure 7. Dependence on NO_y concentration of (a) IEPOX-SOA factor loading, (b) organic mass concentration, and (c) the ratio *f* of the IEPOX-SOA factor loading to the organic PM concentration. Data are segregated by low (< 0.1 μg m^{-3}) and high (> 0.3 μg m^{-3}) sulfate mass concentration and grouped into five levels of NO_y concentration (Figure 6). Squares represent medians of each group. Interquartile ranges are represented by whiskers along the abscissa and shading along the ordinate. The plotted data sets were recorded during local afternoon (12:00-16:00 local time; 16:00-20:00 UTC).

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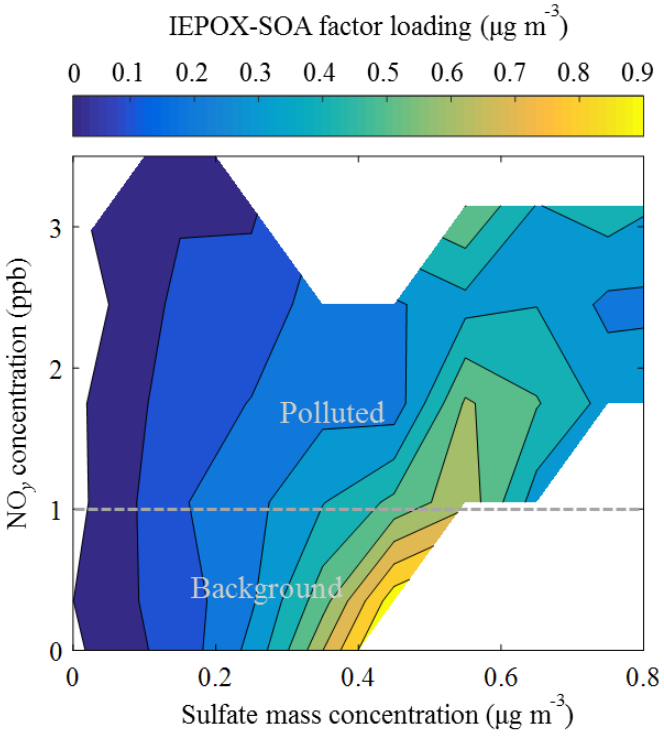

Figure 8. Contours of IEPOX-SOA factor loading for sulfate and NO_y concentrations. The plotted data were recorded during local afternoon (12:00-16:00 local time; 16:00-20:00 UTC). Typical transition between regimes of background and polluted conditions for the region downwind of Manaus are approximately represented by the dashed gray line.

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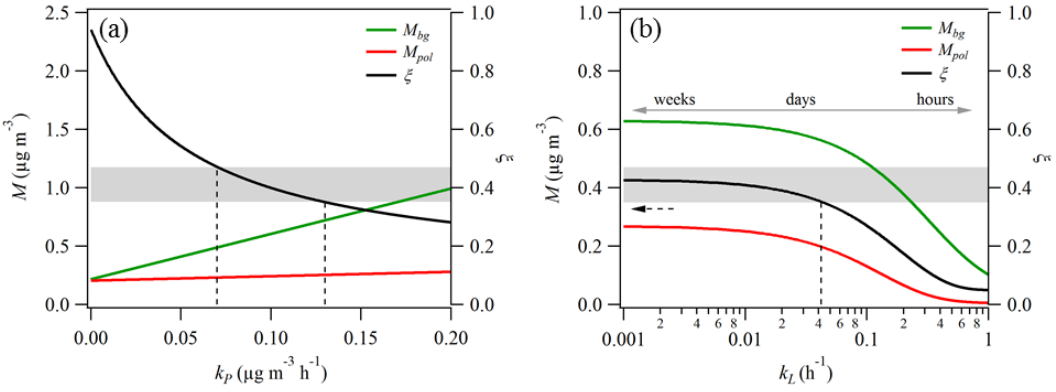

Figure 9. Modeled IEPOX-derived PM mass concentrations M_{pol} and M_{bg} at the T3 site under polluted compared to background conditions. The ratio ξ of concentrations (i.e., M_{pol} /M_{bg}) is also plotted. Panels a and b correspond to the two model Cases 1 and 2 listed in Table 4 and described in the text. Gray shading indicates the range of observed values of ξ across low and high sulfate concentrations. Dashed lines indicate the intersection of modeled and observed values of ξ and the corresponding constrained values of k_P or k_L along the abscissa. Labels above the double-headed arrow in panel b correspond to characteristic times (i.e., k_L^{-1}). The dashed black arrow in panel b communicates that the observed values of ξ provide no constraint on the lower limit of k_L.