

Anthropogenic Impacts on the Atmosphere

Natural and anthropogenically-influenced isoprene oxidation in the Southeastern U.S.A. and central Amazon

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34 ABSTRACT

35 Anthropogenic emissions alter secondary organic aerosol (SOA) formation chemistry from
36 naturally emitted isoprene. We use correlations of tracers and tracer ratios to provide new
37 perspectives on sulfate, NO_x , and particle acidity influencing isoprene-derived SOA in two
38 isoprene-rich forested environments representing clean to polluted conditions—wet and dry
39 seasons in central Amazonia and Southeastern U.S.A. summer. We used the Semi-Volatile
40 Thermal desorption Aerosol Gas Chromatograph (SV-TAG) and filter collection to measure
41 SOA tracers indicative of isoprene/ HO_2 (2-methyltetrols, C_5 -alkene triols, 2-methyltetrol
42 organosulfates) and isoprene/ NO_x (2-methylglyceric acid, 2-methylglyceric acid organosulfate)
43 pathways. Summed concentrations of these tracers correlated with particulate sulfate spanning
44 three orders of magnitude, suggesting that $1 \mu\text{g m}^{-3}$ reduction in sulfate corresponds with at least
45 $\sim 0.5 \mu\text{g m}^{-3}$ reduction in isoprene-derived SOA. We also find that isoprene/ NO_x pathway SOA
46 mass is primarily comprised of organosulfates, $\sim 97\%$ in the Amazon and $\sim 55\%$ in the
47 Southeastern U.S. We infer under natural conditions in high isoprene emission regions,
48 preindustrial aerosol sulfate was almost exclusively isoprene-derived organosulfates, which are
49 traditionally thought as representative of anthropogenic influence. We further report the first
50 field observations showing that particle acidity correlates positively with 2-methylglyceric acid
51 partitioning to the gas phase and negatively with the ratio of 2-methyltetrols to C_5 -alkene triols.

52 **Introduction**

53 Isoprene-derived carbon contributes significantly to the global secondary organic aerosol (SOA)
54 budget.¹ As such it contributes to global impacts of SOA including air quality, adverse human
55 health effects, and affecting Earth's radiative balance. SOA formed from oxidation of biogenic

56 volatile organic compounds (VOCs), such as isoprene, is enhanced by anthropogenic pollutants
57 including NO_x, SO₂, O₃, black carbon, and particulate matter.²⁻⁷ Still, atmospheric measurements
58 constraining chemical mechanisms and understanding of the extent by which these chemical levers
59 affect isoprene-derived SOA formation are limited.⁸⁻¹⁴ The anthropogenic impact of NO_x and SO₂
60 (as a precursor to particulate sulfate) on SOA formation from isoprene has been investigated
61 extensively in the laboratory.^{2,3,15-20} NO_x ultimately controls the branching ratio between different
62 chemical pathways to SOA derived from isoprene (referenced hereafter as isoprene-SOA), and
63 particulate sulfate facilitates the reactive uptake of isoprene-derived gas-phase intermediates.^{5,21-}
64 ²³ Sulfate also affects particle liquid water content and particle pH, all of which affect the
65 physicochemical conditions under which isoprene-SOA forms.^{8,24-29}

66 Isoprene reacts primarily with OH radicals during daytime forming an isoprene peroxy radical.
67 At sufficiently low NO_x levels (referenced as isoprene/HO₂ pathway), an isoprene hydroperoxide
68 (ISOPOOH) is formed, and subsequent oxidation of ISOPOOH with an OH radical results in
69 rearrangement to gas-phase isoprene epoxydiol (IEPOX) isomers.³⁰ Under these conditions,
70 isoprene-SOA derives primarily from acid-catalyzed multiphase chemistry of IEPOX involving
71 uptake into the aqueous phase of particulate matter,^{21,22,27,30-33} and this SOA is referred to as
72 IEPOX-SOA. IEPOX-SOA is estimated to contribute up to 30% of OA across many sites
73 worldwide.^{7,34} Several molecular tracers of IEPOX-SOA previously measured in laboratory/field
74 include: 2-methyltetrols and their oligomers,^{21,35-37} C₅-alkene triols,^{15,16,38,39} methyl
75 tetrahydrofurans, and methyltetrol sulfates.^{5,21,24,40-42} These molecular tracers (all isomers listed
76 **Table S2**) will be respectively referred to in the rest of this paper as: 2-MTs, C5ALKTRIOLS,
77 THFs, and MT-OSs. Oligomers formed from some of these tracers have been observed,¹⁵ although

78 their mass contribution remains unconstrained, and they may decompose during thermal
79 desorption analysis contributing to the observed tracers.^{42–45}

80 The presence of higher levels of NO_x (referenced as isoprene/NO_x pathway) leads to a parallel
81 route of SOA formation from oxidation of methacrolein (MACR),^{17,21,46} referred here as MACR-
82 SOA. Oxidation of MACR forms methacryloyl peroxyoxynitrate (MPAN), which further oxidizes to
83 methacrylic epoxide (MAE)⁴⁷ and hydroxyl methyl methyl lactone (HMML).⁴⁸ Multiphase
84 chemistry of MAE/HMML leads to 2-methylglyceric acid (2-MG), 2-methylglyceric acid
85 organosulfate (2-MG-OS), and their respective oligomeric forms.^{15,49,50} This route is typically less
86 efficient in SOA formation compared to IEPOX-SOA route because MPAN survival in the
87 atmosphere is strongly enhanced at lower temperatures while isoprene emissions increase
88 exponentially with temperature. Thus, reaction with OH must occur on a timescale competitive to
89 MPAN decomposition to sufficiently form MACR-SOA intermediates.⁵¹

90 Field observations spanning clean to polluted conditions are sparse³⁶ but important for
91 examining correlations between molecular markers of isoprene-SOA and chemical levers on OA
92 chemistry (e.g. NO_x, particulate sulfate, and particle pH). Here, we made measurements in two
93 similar, though unique environments (Southeast United States and central Amazon) to examine
94 isoprene chemistry over such atmospheric conditions. Each region is high in isoprene emissions,
95 yet with differing histories and trajectories of anthropogenic influence. Previous measurements in
96 another region of the Amazon Basin (Rondônia, Brazil) included offline filter-based measurement
97 of isoprene/HO_x tracers, 2-MTs and C5ALKTRIOLS.³⁶ Here we report in situ measurement of
98 these tracers in addition to isoprene/NO_x tracer 2-MG in both gas and particle phases, as well as
99 offline filter-based measurements of isoprene-derived organosulfates, MT-OSs and 2-MG-OS.
100 Through correlation analyses utilizing this newly available higher time resolution tracer and

101 particle composition data, we further specify the role of particle acidity and the extent by which
102 anthropogenically- *and* naturally-derived NO_x and sulfate promote their formation, affect tracer
103 ratios, and determine their gas/particle partitioning.

104 **Materials and Methods**

105 This work relies primarily on data collected using a Semi-Volatile Thermal desorption Aerosol
106 Gas Chromatograph (SV-TAG) and a suite of supporting instrumentation at two field sites over
107 three campaigns. Measurements were conducted at the Centreville, Alabama, U.S.A. site during
108 the Southern Oxidant and Aerosol Study 2013 (SOAS)⁵² and downwind of Manaus, Brazil “T3”
109 site during the Green Ocean Amazon (GoAmazon 2014/5) field campaigns.^{53,54} SOAS took place
110 from 1 Jun 2013 to 15 Jul 2013. For GoAmazon 2014/5, measurements reported herein took place
111 from 1 Feb to 26 Mar 2014, known as the first Intensive Operating Period 1 (IOP1) and referred
112 to hereafter as “wet season”, and from 15 Aug to 15 Oct 2014, known as IOP2 and referred to
113 hereafter as “dry season.” Both sites represent areas of high isoprene emissions affected by urban
114 centers (i.e. Birmingham, Alabama, for Centreville and Manaus, Amazonas for “T3”). Manaus
115 plume impacted sampled air masses at “T3” ~40% (wet season) and ~60% (dry season) of the
116 time. The dry season is further characterized by an enhancement in regional biomass burning
117 influences.^{54,55}

118 SV-TAG provided gas and particle phase speciation of semi-volatile organic compounds, an
119 Aerodyne Aerosol Mass Spectrometer (AMS) provided PM₁ organic and inorganic speciation, and
120 quartz filter analysis provided speciation of OSs in PM_{2.5} samples collected during SOAS and PM₁
121 filter samples collected during GoAmazon. An Ionicon Proton Transfer Mass Spectrometer
122 (PTRMS) measured gas-phase concentrations of isoprene. Instrument operation, analysis, and

123 deployment details during these field campaigns were published for SV-TAG,^{43,56,57} AMS,^{13,58,59}
124 particulate filter collection and OSs analysis by liquid chromatography coupled to electrospray
125 ionization high-resolution mass spectrometry (LC/ESI-HR-MS),^{14,57,60,61} and PTRMS.^{62,63}
126 Synthesized MT-OSs were analyzed by SV-TAG to estimate degree of their decomposition during
127 analysis; roughly < 10% of measured 2-MTs and C5ALKTRIOLs are formed through
128 decomposition of MT-OSs, for details see Supporting Information. Model results for particle pH
129 and liquid water content (LWC) are the same as used by Isaacman-VanWertz et al.,⁴³ utilizing the
130 thermodynamic model ISORROPIA-II.⁶⁴ During SOAS, meteorological data (temperature,
131 relative humidity, wind direction) and concentrations of NO_x, NO_y, and O₃ were measured within
132 the SouthEastern Aersol Research and Characterization Network (SEARCH).⁶⁵ During
133 GoAmazon, these parameters were measured within the co-located U.S. Department of Energy
134 Atmospheric Radiation Measurement Climate Facility comprising Atmospheric Radiation
135 Measurement Facility One (AMF-1) and Mobile Aerosol Observation System (MAOS).⁶⁶

136 **Results and Discussion**

137 **1. Field campaign comparisons**

138 Concentration ranges from GoAmazon wet/dry season and SOAS for isoprene, PM₁ organic,
139 sulfate, and daytime NO_y (representative of photochemical conditions and processed NO_x) are
140 summarized (**Figure S1**). GoAmazon wet season median concentrations are lowest, representing
141 the least polluted and lowest aerosol loading conditions, though median NO_y was only slightly
142 lower with similar range as other measurement campaigns. GoAmazon dry season is characterized
143 with higher biogenic emissions, regional biomass burning emissions, and less wet deposition,⁵⁵
144 having highest PM₁ organic although between wet season and SOAS for isoprene and sulfate.

145 SOAS exhibits highest anthropogenic influence (sulfate) and highest isoprene concentrations.
146 Median NO_y concentration during SOAS is slightly higher than the other campaigns, though
147 narrow in range suggesting fewer large local emission sources and a more regionally averaged
148 contribution sampled in this rural region of Alabama. The greater range of observed NO_y values
149 during GoAmazon reflects pollution plumes influencing local chemistry.⁶⁷ We note that while
150 more polluted on average than GoAmazon, SOAS pollution levels were in fact the lowest since
151 measurements began in 1999 for that region.⁶⁸ Mean temperature (T) and relative humidity (RH)
152 during corresponding measurement times were: SOAS $T_{\text{mean}} = 24.7\text{ }^\circ\text{C}$, $\text{RH}_{\text{mean}} = 82\%$; GoAmazon
153 wet season $T_{\text{mean}} = 26.5\text{ }^\circ\text{C}$, $\text{RH}_{\text{mean}} = 90\%$; GoAmazon dry season $T_{\text{mean}} = 27.9\text{ }^\circ\text{C}$, $\text{RH}_{\text{mean}} = 83\%$.⁴³

154 2. Tracer correlations reveal chemical factors influencing isoprene chemistry

155 The range of conditions for biogenic and anthropogenic emissions observed in these campaigns
156 provides a useful opportunity to compare the chemical fate of isoprene during oxidation under
157 clean versus polluted conditions. Temporal variability in SV-TAG measured molecular markers
158 (particle-only and gas + particle) were compared with each other and several other
159 calculated/measured parameters through correlation analyses. Coefficients of determination, R^2 ,
160 are summarized in **Table S3** for: SOAS; GoAmazon wet season; GoAmazon dry season; all
161 datasets taken together. Many moderate correlations ($R^2 \geq 0.4$, values bolded in **Table S3**)
162 between measured tracers and organic, sulfate, nitrate, and ozone concentrations within any one
163 deployment period exist. When measurements from SOAS and both GoAmazon deployments are
164 taken together, correlations for IEPOX-SOA tracers are still clearly strongest with sulfate ($R^2 =$
165 0.40). Taken individually, correlations of molecular markers of IEPOX-derived SOA tracers (i.e.
166 2-MTs, C5ALKTRIOLS) with sulfate during GoAmazon are generally higher than previous
167 analyses for other sites throughout the U.S.A.^{11,58} This could derive from 1) owing to hourly

168 measurements by SV-TAG, increased time resolution may better capture dynamics of particle
169 composition, and 2) a wide range in sulfate concentrations was measured across these
170 deployments, revealing correlation with sulfate is strong across the whole range from polluted to
171 extremely clean conditions, not just when anthropogenic pollution is abundant. Correlations of
172 tracers with particle pH and liquid water content (LWC) vary across different deployments from
173 non-existent to moderate, and we further discuss these relationships in the context of isoprene-
174 SOA formation.

175 **2A. Influence of sulfate on isoprene-SOA from clean to polluted conditions**

176 Many studies interpret enhancements in isoprene-SOA formation correlated with sulfate as
177 indicative of isoprene-SOA formation enhanced by anthropogenically-derived sulfate.^{2,9,10,69}
178 Sulfate is cited as having a central role on influencing SOA formation from isoprene by enhancing
179 uptake of IEPOX/MAE/HMML into the particle phase by affecting particle surface area,⁶⁹ as well
180 as hygroscopicity and thereby LWC, aqueous particle volume,^{12,29,70,71} and particle acidity.^{21,24,27,47}
181 It can also facilitate “salting in” conditions to enhance IEPOX uptake into the particle phase and
182 directly reacts with epoxide intermediates to form organosulfates,^{5,47} whereas the free acid form
183 (sulfuric acid) serves as a catalyst in the hydrolysis of IEPOX to form 2-MTs.^{9,33} It was surmised
184 that sulfate is the limiting reagent in isoprene-SOA formation in the Southeast U.S.A. based on
185 significant correlation between sulfate and estimated isoprene-derived SOA (positive matrix
186 factorization analysis of AMS mass spectra).^{9,34} While yields of several isoprene SOA molecular
187 markers increases in the presence of particulate sulfate in acidic particles, atmospheric
188 measurements reporting such strong correlations are limited to regions with significant
189 anthropogenic pollution such as eastern U.S.A. and China.^{10,11,72}

190 Here, we show that markers of both IEPOX-SOA and MACR-SOA correlate with ambient
191 sulfate, but over a range of concentrations covering much cleaner conditions than previously
192 reported.^{9,13,51,58} Molecular tracers are well correlated even at concentrations of particulate sulfate
193 $< 0.5 \mu\text{g m}^{-3}$ (**Figure 1**) representing Amazon basin background conditions and at times pre-
194 industrial conditions.^{13,73–75} In these environments, IEPOX-SOA tracers (2-MTs +
195 C5ALKTRIOLS) (**Figure 1a**) contribute significantly more mass to SOA than MACR-SOA tracer
196 (2-MG) (**Figure 1b**). IEPOX-SOA tracers correlate moderately with sulfate across all three
197 campaigns (**Table S3**: $R^2 = 0.48; 0.49; 0.57; 0.40$ for SOAS; wet season; dry season; all datasets,
198 respectively), similar to or higher than previous reports of tracers^{10,11} and IEPOX-SOA statistical
199 factor.^{9,13,29,34} 2-MG contributes more mass in SOAS data than GoAmazon but is only weakly
200 correlated with sulfate during all campaigns (**Table S3**: $R^2 < 0.25$ for each dataset). We keep in
201 mind that correlations can also be affected by atmospheric transport including dispersion/dilution
202 and wet deposition. Despite marginal correlation between 2-MG and sulfate and the offset in
203 magnitude between SOAS and GoAmazon, we demonstrate that correlations are improved by
204 accounting for OS formations.

205 **2B. OS formations differ by HO_2/NO_x pathway and environment**

206 OSs formed from chemical reaction of isoprene-derived intermediates and sulfate in the aqueous
207 phase contribute a substantial fraction of isoprene-SOA.^{14,41,42,61,76–78} Here, OS analysis included
208 MT-OSs from IEPOX (“OS-216”),^{5,21,22} and 2-MG-OS (“OS-200”), which can be derived along
209 MACR-SOA (isoprene/ NO_x) pathway from 2-MG⁵ and HMML/MAE.⁴⁷ We explore the relative
210 distribution of the isoprene-derived SOA organic carbon mass in molecular tracers measured by
211 SV-TAG, versus OS forms (offline filter analysis).

212 Summed particle-phase isoprene-SOA tracers (SV-TAG molecular tracers and OSs organic
213 carbon) contribute on average 11%, 13%, and 14% of total PM_{10} organic mass for SOAS,
214 GoAmazon wet season, and GoAmazon dry season, respectively. **Figure 2** shows the distribution
215 of isoprene-SOA tracers, including OSs across the three deployments. For IEPOX-SOA pathway,
216 similar fractions as MT-OSs are present across all campaigns (23-28%), leading to similar trends
217 between data in **Figure 1a** and **Figure 1c** (summation of 2-MTs, C5ALKTRIOLS, and MT-OSs
218 organic carbon) but with a vertical offset. Similar correlation with sulfate (**Table S3**; $R^2 = 0.41$
219 accounting for OSs vs $R^2 = 0.40$ excluding OSs) is observed. **Figure 2** shows that MACR-SOA
220 pathway is only a few percent of observed isoprene-SOA. However, most MACR-SOA pathway
221 mass during GoAmazon is bound with sulfate as 2-MG-OS, whereas in SOAS the distribution is
222 almost even between 2-MG and 2-MG-OS. Thus, combining 2-MG-OS organic mass with 2-MG
223 (**Figure 1d**) increases total accounted MACR-SOA by more than an order of magnitude for
224 GoAmazon data than that accounted in **Figure 1b**, revealing sulfate as an important nucleophile
225 in MACR-SOA formation as well. Accounting for GoAmazon 2-MG-OS carbon, correlation of
226 MACR-SOA tracers with sulfate (**Table S5**; $R^2 = 0.33$) is slightly improved (**Table S3**; $R^2 < 0.25$
227 each dataset), comparable to previous reports ($R^2 \leq 0.33$),^{10,11,72} but extended here to levels of
228 sulfate $< 1 \mu\text{g m}^{-3}$. The correlation is in fact much stronger than previous reports^{10,11,72} if data with
229 sulfate $\leq 1 \mu\text{g m}^{-3}$ are considered (**Table S5**; $R^2 = 0.66$), as there may be a threshold in MACR-
230 SOA at $>1 \mu\text{g m}^{-3}$ sulfate concentrations. In contrast, there is no apparent threshold for IEPOX-
231 SOA over the sulfate concentrations observed. Since previous observations of MACR-SOA
232 correlation with sulfate are typically reported for conditions with sulfate concentrations $> 1 \mu\text{g m}^{-3}$,
233 this could be why the role of sulfate on MACR-SOA pathway has been less clear by R^2 . Further,
234 although sulfate and 2-MG levels are higher during SOAS than during GoAmazon (**Figure S1** and

235 **Figure 1**), lower 2-MG-OS fraction may result from higher sulfate and free acidity in hydrated
236 particles leading to hydrolysis of 2-MG-OS to 2-MG.⁴⁸ With increasing acidity, 2-MG partitions
237 to the gas phase (see Section 3A.), which may weaken the correlation with higher sulfate levels.
238 Additional differences might include the relative yields of HMML/MAE formed from MACR⁷⁹ as
239 2-MG precursors, phase state, morphology, or viscosity.

240 Linear regressions of data across all three deployments reflect different relationships between
241 the IEPOX-SOA and MACR-SOA pathways with sulfate (**Figure 1**). Data in **Figure 1** were
242 binned (five data points each), and a linear fit was performed on the means of all bins (**Figure S2**;
243 **Table S4**; **Table S5**). Tracers of both formation pathways correlate with sulfate (IEPOX-SOA:
244 slope = 490.73 ± 35 , $R^2 = 0.88$; MACR-SOA: slope = 5.70 ± 1.28 , $R^2 = 0.59$). Units of slopes are
245 ng m^{-3} of IEPOX or MACR-SOA tracers, respectively, per $\mu\text{g m}^{-3}$ of particulate sulfate.
246 GoAmazon data are situated within fairly distinct ranges of sulfate with little overlap (**Figure 1**).
247 SOAS data, while typically within sulfate $> 1 \mu\text{g m}^{-3}$, does show a similar trend down to lower
248 sulfate levels overlapping GoAmazon data for the case of IEPOX-SOA, but there is very little
249 overlap in measurements from different deployments $< 1 \mu\text{g m}^{-3}$ sulfate for MACR-SOA.

250 From an air quality perspective assuming that sulfate is a primary driver of isoprene-SOA
251 formation,^{5,9,10,34,58,69,80} these quantitative relationships suggest that every $1 \mu\text{g m}^{-3}$ reduction in
252 sulfate can lead to at least $\sim 0.5 \mu\text{g m}^{-3}$ reduction of these tracers contributing to isoprene-SOA, at
253 least over sulfate and NO_y ranges observed here. Previous studies for Southeast U.S.A. also
254 suggested that reductions in SO_2 (taken as reductions in sulfate) lead to significant decreases in
255 SOA⁸¹ from isoprene.^{9,12,26,29,69} This idea is extended here to the measurements taken during
256 GoAmazon wet season characterized by relatively low levels of sulfate, which can represent pre-
257 industrial conditions, suggesting that natural sources of SO_2 also control SOA yield from isoprene

258 oxidation. For the Amazon basin, low “background” sulfate levels can be attributed to biogenic
259 sources such as DMSO and H₂S as well as long range transport of (anthropogenic) sulfate
260 sources.^{13,73,75,82,83} Higher sulfate levels were observed during GoAmazon dry season, some
261 attributable to biomass burning⁸⁴ and not due to seasonal changes in anthropogenic activity at
262 Manaus. We surmise that sulfate concentrations are higher relative to the wet season in part
263 because there is less wet deposition due to precipitation and lower ventilation rates in the dry
264 season. In contrast, higher concentrations of sulfate (some similar to levels observed during dry
265 season of central Amazon) observed in the Southeast U.S.A. are reasonably attributable to
266 anthropogenic activity.^{68,85}

267 Overall, these results further corroborate aerosol sulfate as a strong determinant of isoprene-
268 SOA formation over a wide range of environments. Importantly, though we find this correlation
269 holds across three orders of magnitude down to low levels likely representative of pre-industrial
270 conditions and revealed here to be true for the isoprene/NO_x channel as well. While 2-MG-OS at
271 SOAS is a reflection of anthropogenic influence from NO_x and SO₂ emissions, natural NO_x
272 emissions in the Amazon are sufficient to sustain isoprene/NO_x pathways to form MACR-SOA
273 during the wet season.⁶³ This suggests that even background/natural isoprene-derived SOA is
274 enhanced by natural sulfate, and that sulfate is likely the limiting reagent given plenty of gas-phase
275 production of IEPOX and HMML/MAE for the isoprene/HO₂ and isoprene NO_x channels,
276 respectively. As Riva et al.¹⁴ suggest for pristine central Amazon conditions, over 80% of inorganic
277 sulfate converts to organosulfur via reaction with IEPOX. Further, GoAmazon particles can be
278 more acidic compared to areas with greater anthropogenic NH₃(g) emissions, promoting relatively
279 greater OS formation from isoprene.⁶¹ Thus, we infer that under natural conditions in regions with
280 high isoprene emissions, preindustrial aerosol sulfate was likely almost exclusively OSs derived

281 from isoprene. Because OS and inorganic sulfate differ in water uptake properties,^{86,87} this implies
282 preindustrial aerosol sulfate (albeit less abundant) may have been less reflective than current
283 models assume.

284 3. Role of particle acidity

285 While sulfate is known to affect and correlate with particle pH (**Figure S3**), the separate
286 influence of particle acidity on isoprene-SOA formation remains unclear. Laboratory studies
287 demonstrated particle acidity enhances IEPOX uptake^{24,27} and MACR-SOA.^{48,88} Higher dry
288 season IEPOX-SOA tracers concentrations compared to those in wet and transition seasons of
289 2002 in another region of the Amazon Basin were attributed in part to increased aerosol acidity by
290 contrasting concentrations of acidic gases, sulfate, and nitrate anions.³⁶ Online measurements of
291 PM₁ composition conducted here now allow for explicit correlations of these tracers with pH,
292 though they are not found to be significantly correlated, (**Table S3**), nor are appreciable differences
293 in particle acidity between the seasons observed (**Figure S3**). This further supports that sulfate is
294 a primary driver of the observed tracers concentrations as discussed before. Other field
295 measurements of isoprene-SOA molecular markers show no significant correlations with
296 calculated pH,^{10,11,51,89} often ascribed to measurements within a small pH range and possible
297 conflating effects of regional transport where calculated pH for conditions at a field site are not
298 necessarily representative of aerosol acidity at the time/place where pH-dependent chemistry
299 occurs. We also do not observe significant correlations between concentrations of individual
300 IEPOX-SOA and MACR-SOA markers and pH (**Table S3**), except slight to moderate correlation
301 when considering gas + particle 2-MG ($R^2 = 0.45$; 0.37 for wet season; dry season). This revealed
302 that for isoprene/NO_x pathway, the distribution of 2-MG between gas and particle phases correlates

303 with pH. For isoprene/HO₂ pathway, we later reveal correlation between pH and the ratio of
304 IEPOX-SOA markers, 2-MTs and C5ALKTRIOLS.

305 **3A. Particle acidity and liquid water content affects MACR-SOA phase distribution**

306 **Figure 3** shows that 2-MG mass fraction in particle phase, F_p , correlates with pH during
307 GoAmazon dry season ($R^2 = 0.55$). The particle-phase concentration is in fact relatively constant
308 over a range of pH values (0-3) for all three datasets (**Figure S4**). However, when considering
309 gas-phase concentration, calculated as the difference between SV-TAG total (gas + particle) and
310 particle channels, there is a decrease with increasing pH most obvious during GoAmazon (**Figure**
311 **S5**). That is, 2-MG increasingly partitions to gas phase with increasing acidity. No/weak
312 correlations of 2-MG with acidity have otherwise been observed from other field studies in the
313 U.S.A.,^{8,10,11,51} possibly due to methods of utilizing filter-based measurements which can suffer
314 from artifacts of gas-phase adsorption, averaging due to lower time-resolution, as well as field
315 observations that typically fall within narrow pH ranges (often below pH=2). SOAS data lay in a
316 narrow range of calculated pH (0.25-1.0) and exhibit wider variation though higher average F_p
317 values for the same pH range as in GoAmazon (**Figure 3**). The variation may be due to other
318 factors of liquid water content, ion activity, organics, and phase that affect 2-MG accommodation
319 for SOAS conditions. More highly viscous and coated organic particles could lead to less 2-MG
320 repartitioning back to the gas phase, keeping F_p values higher than expected from 2-MG vapor
321 pressure.⁴³ In contrast, GoAmazon conditions comprise wider ranges in particle acidity and LWC
322 associated with changes in 2-MG concentrations and observed F_p . The strongest trend for SOAS
323 2-MG is with LWC (**Figure S6**) revealed in the total (gas + particle) channel; total 2-MG decreases
324 with increasing LWC, again mostly associated with a decreasing gas-phase concentration as
325 associated decreases in particle phase 2-MG are more modest (**Figure S7**). These measurements

326 are first field observation of pH- and LWC-dependent 2-MG accommodation in accordance to
327 laboratory measurements,⁴⁸ in which gaseous 2-MG concentrations were observed to increase in
328 the headspace over increasingly acidic solutions. This also suggests that for particles that are more
329 acidic, more carbon through MACR-SOA pathway recycles back to the gas-phase after
330 MAE/HMML uptake if no limitations to gas-particle exchange exist. In other words, the extent to
331 which the particle phase acts as a reservoir of NO_x-derived organic species is pH dependent for
332 GoAmazon conditions. This further implies that PM formation along this route may be minimized
333 by decreasing particle pH as Nguyen et al.⁴⁸ proposed that hydrated particles with higher free
334 acidity might favor monomeric 2-MG as well as hydrolyze sulfate and nitrate esters⁷⁹ leading to
335 suppression of SOA growth. Still, many other SOA formation mechanisms are more efficient
336 under acidic conditions.⁹⁰ Others demonstrate that while SO₂ controls have led to lower particulate
337 sulfate in the Southeast U.S.A., PM has remained acidic.^{68,91} While GoAmazon includes pre-
338 anthropogenic sulfate levels much lower than those of SOAS, and can be more acidic (associated
339 with higher gas-phase fraction of 2-MG), they are still sufficiently acidic to promote IEPOX and
340 MAE/HMML uptake as well as 2-MG-OS formation. This suggests that isoprene-SOA formation
341 from these pathways is sustained even under natural/background levels of sulfate and NO_x, and
342 control of anthropogenic SO₂ emissions (as a source of sulfate) remains most effective in limiting
343 SOA formation from both pathways.

344 **3B. Tracer ratios correlations further reveal role of acidity**

345 To better understand chemical controls on distribution of isoprene-derived carbon between
346 different pathways to isoprene-SOA formation, we examine ratios of the SV-TAG measured
347 molecular tracers as correlated with other chemical parameters. In this section we do not include
348 carbon associated with OSs because of coarser time resolution of these measurements that would

349 limit the robustness of correlations; we note that scaling tracer concentrations by an average OS
350 contribution would not impact correlations. We first investigate isoprene/HO₂ pathway (i.e.
351 summed 2-MTs and C5ALKTRIOLS) vs the isoprene/NO_x pathway (i.e. 2-MG) as IEPOX-SOA
352 markers:MACR-SOA markers. We further explore branching of IEPOX-SOA carbon between 2-
353 MTs and C5ALKTRIOLS.

354 **3C. Isoprene/HO₂ vs Isoprene/NO_x pathway tracers correlations**

355 Based on current understandings of isoprene + OH oxidation, it would be expected that the split
356 between carbon associated with IEPOX-SOA and MACR-SOA pathways would be NO_y
357 dependent. We evaluate the ratio of IEPOX-SOA:MACR-SOA tracers, i.e. (2-MTs +
358 C5ALKTRIOLS):(2-MG), as correlated with NO_y. Using NO_y as a surrogate for integrated
359 exposure of sampled air masses to NO_x^{13,63,67} we explore the IEPOX-SOA:MACR-SOA tracers
360 ratio as a proxy for the branching ratio between isoprene/HO₂ vs isoprene/NO_x pathways. While
361 this ratio might be expected to decrease with increasing NO_y, correlations were poor regardless of
362 phase (**Table S3**). **Figure S8** (particle phase) and **Figure S9** (total) also show that IEPOX-
363 SOA:MACR-SOA ratios vs NO_y filtered for daytime hours are still poorly correlated and widely
364 variable across deployments. Very weak, though higher R² values (~0.2 for GoAmazon) are found
365 for IEPOX-SOA:MACR-SOA ratios vs O₃ (**Table S3**), consistent with total 2-MG correlating
366 better with O₃ (R² > 0.3 and up to 0.66) than with NO_y (no correlation). Correlation of 2-MG with
367 O₃ (**Figure S10** and **Figure S11**) suggests that O₃ is a better indicator of air mass age than NO_y and
368 is further discussed in Supporting Information.

369 **3D. Isoprene/HO₂ tracers ratio is pH dependent**

370 Limited studies have probed chemical controls on relative yields of IEPOX-SOA tracers, 2-MTs
371 and C5ALKTRIOLS.^{21,23,71} Formation of C5ALKTRIOLS has been explained by acid-catalyzed
372 ring opening of isoprene epoxydiols.³⁸ Recent work suggests some fraction derives from
373 decomposition of OSs and their oligomers thereof in some analytical techniques,⁴² which may be
374 representative of a tendency for many of these tracers to be formed by (thermal) decomposition
375 during analysis.^{44,45,92} Testing of MT-OSs in SV-TAG (see Supporting Information) suggests they
376 would be a minor contribution (< 10% by mass) to 2-MTs and C5ALKTRIOLS observed here.
377 The extent to which a given compound represents a sampled atmospheric constituent versus a
378 transformed product of analysis remains an active area of methodological research. Here, we use
379 these tracers as useful known indicators of isoprene oxidation, and we evaluate the extent to which
380 different compound classes represent different formation pathways and can provide insight into
381 particle-formation chemistry.

382 Plots of 2-MTs vs C5ALKTRIOLS reveal that distribution of IEPOX-derived carbon (as inferred
383 from slope of the best fit line) and correlation between these analytes varies across these
384 deployments **Figure 4**. 2-MTs:C5ALKTRIOLS is 0.52 with $R^2=0.16$ for SOAS (**Figure 4a**), 0.27
385 with $R^2 = 0.54$ for GoAmazon wet season (**Figure 4b**), and 0.17 with $R^2 = 0.72$ for GoAmazon
386 dry season (**Figure 4c**). The variability in ratio and correlation of these tracers indicate that these
387 analytes derive from distinct chemical conditions and possibly from additional precursors besides
388 IEPOX. For example, 2-MTs were observed in SOA generated from isoprene ozonolysis under
389 laboratory conditions,^{60,93} though correlations of 2-MTs with O_3 are too poor in these datasets to
390 suggest it as a leading source (**Table S3**).

391 The strongest explanatory variable for 2-MTs:C5ALKTRIOLS is pH ($R^2=0.14$ for GoAmazon
392 wet season, $R^2 = 0.42$ for GoAmazon dry season, **Table S3** and **Figure 4d**). No trend with pH is

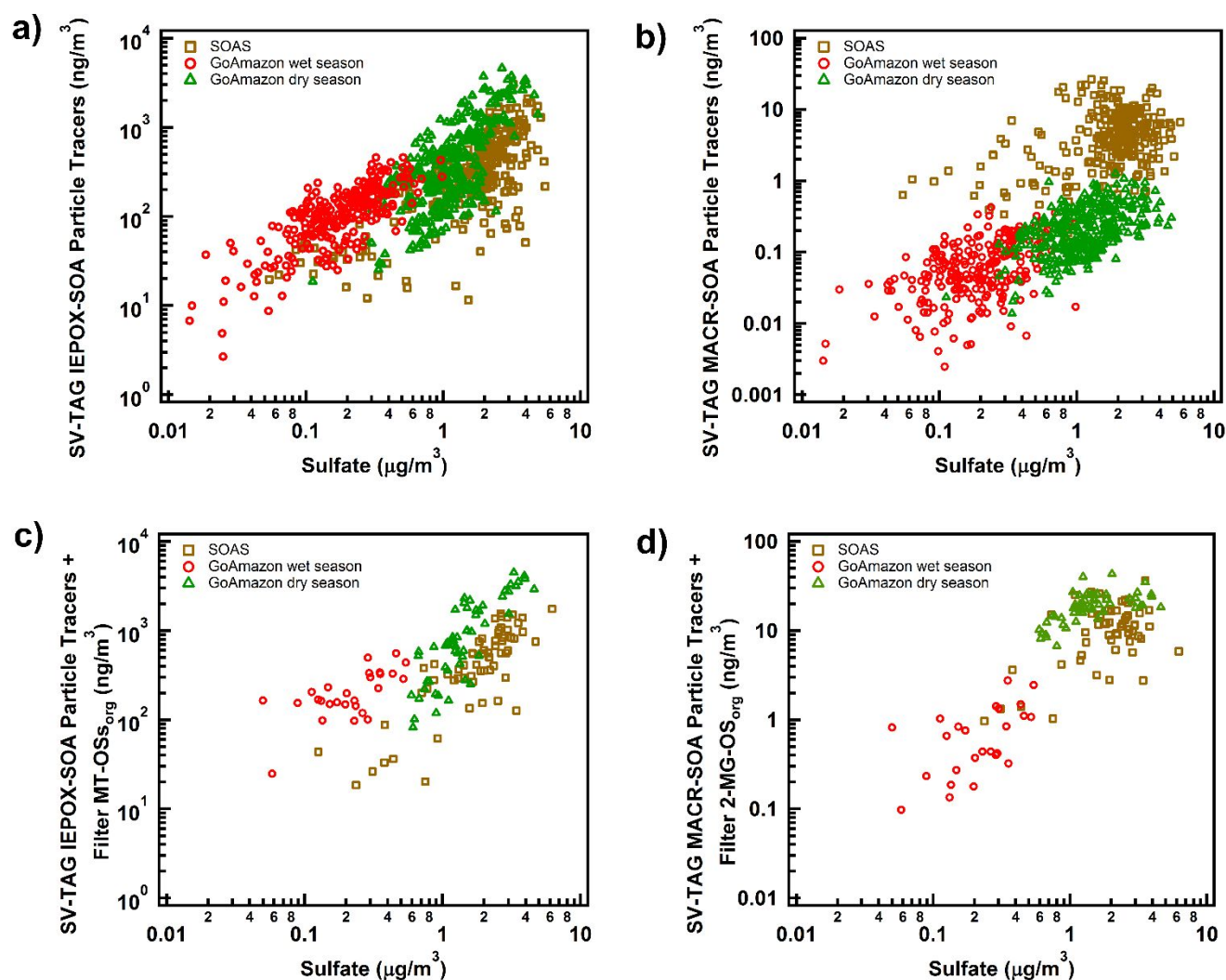
393 observed for SOAS and most data fall within $\text{pH} = 0.5 \pm 0.5$. This correlation was most obvious
394 in GoAmazon datasets (**Figure 4**), where particle pH ranges more widely (0-3). As pH decreases,
395 2-MTS:C5ALKTRIOLS also decreases suggesting that C5ALKTRIOLS formation is enhanced
396 with increasing particle acidity (**Figure 4d**).³⁸ It is important to note that pH is a modeled output,
397 and we keep in mind that the calculated pH values here result from assuming instantaneous gas-
398 particle equilibrium. This assumption seems valid for liquid-phase organic aerosols observed in
399 GoAmazon⁹⁴ and SOAS.⁹⁵ While RH and hence LWC can be highly variable as particles move
400 about in daytime turbulence within the boundary layer, modeled pH may not reflect pH when
401 IEPOX-SOA markers actually form, as limitations of the calculation have been discussed.^{13,43}
402 Still, we find that it is a useful metric for assessing particle-phase chemical conditions at the time
403 these markers are measured. That is, concerted effects of RH, T , and gas/particle composition (e.g.
404 sulfate, LWC, organics) is captured in calculated pH, and 2-MTS:C5ALKTRIOLS ratio serves as
405 useful indicator of IEPOX-SOA formed under varying chemical conditions.

406 **Atmospheric Implications**

407 We provide the first ambient measurements revealing strong correlations with pH impacting
408 tracer ratios derived in the isoprene/ HO_2 pathway (allowing for mechanistic insight) and phase
409 partitioning of the isoprene/ NO_x pathway tracer, 2-methylglyceric acid. Further, while the role of
410 sulfate in isoprene-SOA formation has been studied, it has primarily been interpreted as a role of
411 anthropogenically-derived sulfate enhancing SOA formation. We show here by contrasting SOAS
412 and GoAmazon, that naturally-derived sulfate also enhances isoprene-SOA formation. In
413 particular, the relatively greater incorporation of naturally-derived sulfate into organosulfates
414 under the isoprene/ NO_x channel during GoAmazon highlights the impact of more highly acidic
415 particle conditions found in an environment representative of pre-industrial conditions, as well as

416 the fact that sulfate may be a stronger nucleophile than previously revealed for this
417 pathway. Organosulfates are typically interpreted as markers of anthropogenic influence on SOA
418 formation, which we demonstrate is not always the case, with implications for how such
419 compounds are represented in global models of SOA and for the chemical composition and
420 properties of pre-industrial SOA.

421 FIGURES



422

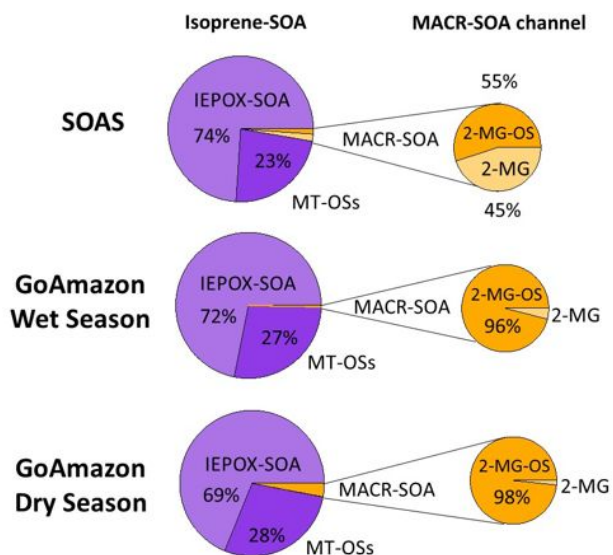
423 **Figure 1.** Particle-phase tracers from a) IEPOX and b) MACR channels of isoprene-SOA
424 formation as measured by SV-TAG and associated particulate sulfate as measured by AMS during
425 SOAS (brown squares), GoAmazon wet season (red circles), and GoAmazon dry season (green
426 triangles). Coefficients of determination, $R^2 = 0.48; 0.49; 0.57; 0.40$ for SOAS; GoAmazon wet
427 season; GoAmazon dry season; all datasets, respectively, for a) IEPOX-SOA tracers correlated
428 with sulfate. $R^2 < 0.25$ for each individual dataset and all datasets taken together for b) MACR-
429 SOA tracers correlated with sulfate. Summation of c) SV-TAG IEPOX-SOA particle-phase

430 tracers and filter MT-OSs organic and d) SV-TAG MACR-SOA particle-phase tracers and filter

431 2-MG-OS organic.

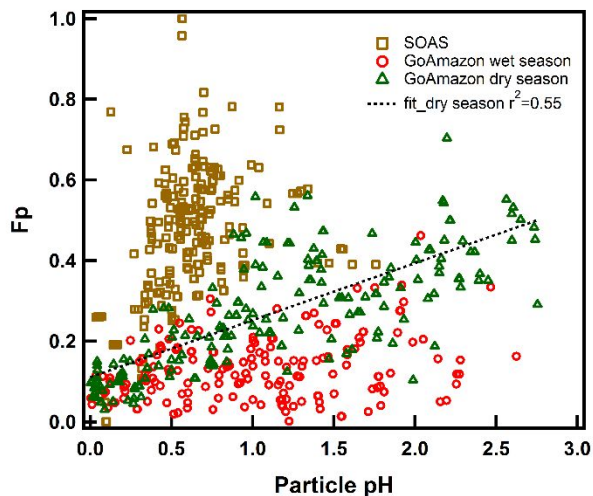
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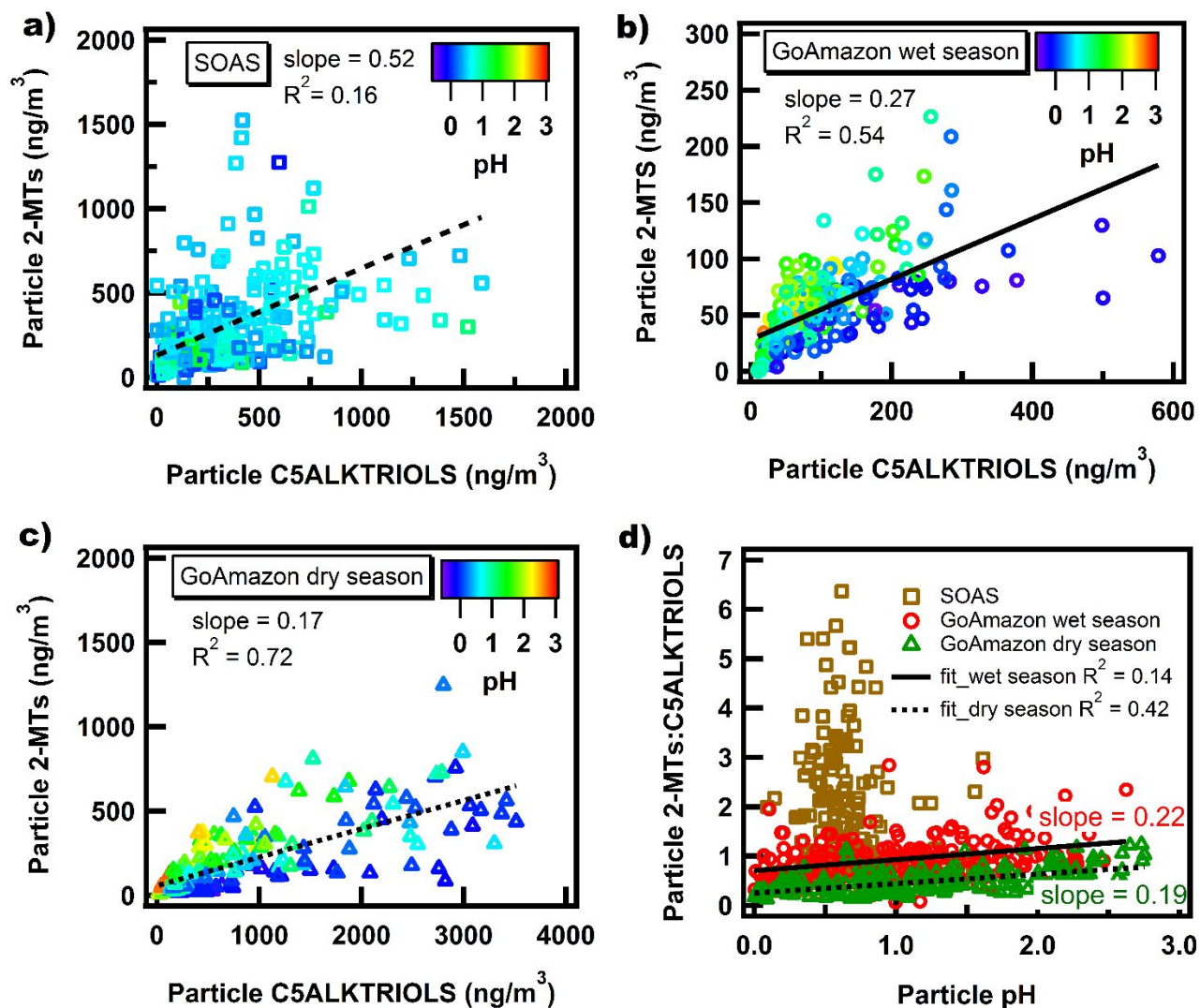


434
 435 **Figure 2.** Distribution of isoprene-derived SOA mass between IEPOX-SOA (purple) molecular
 436 tracers: 2-MTs, C5ALKTRIOLS, and MT-OSs, and MACR-SOA (orange) molecular tracers: 2-
 437 MG and 2-MG-OS for SOAS (top), GoAmazon wet season (middle), and GoAmazon dry season
 438 (bottom).

439



440
441 **Figure 3.** Fraction of 2-MG in particle phase and associated particle pH during SOAS (brown
442 squares), GoAmazon wet season (red circles), and GoAmazon dry season (green triangles). Data
443 smoothed using a running-median smoothing algorithm. Best fit line (dashed) for GoAmazon dry
444 season shown with slope = 0.14, $R^2 = 0.55$. Best fit lines for other campaigns not shown due to
445 poor correlations ($R^2 < 0.2$).



446
 447 **Figure 4.** Particle phase 2-MTs vs C5ALKTRIOLS during a) SOAS, b) GoAmazon wet season,
 448 and c) GoAmazon dry season. Best fit lines for each dataset shown along with slope and R²
 449 values. Data are colored by particle pH, revealing some correlation of 2-MTs: C5ALKTRIOLS
 450 with pH for GoAmazon datasets. Ratio of particle phase 2-MTs and C5ALKTRIOLS vs particle
 451 pH in panel d) for SOAS (brown squares), GoAmazon wet season (red circles), and GoAmazon
 452 dry season (green triangles). Best fit lines for GoAmazon wet season, solid line, slope = 0.22, R²
 453 = 0.14 and GoAmazon dry season, dotted line, slope = 0.19, R² = 0.42 shown.

454 ASSOCIATED CONTENT

455 **Supporting Information.** The Supporting Information is available free of charge.

456 Additional details of Materials and Methods, figures of campaign comparisons, select tracer
457 correlations, and a complete table of coefficients of determination for all calculated tracer
458 correlations are included. (PDF)

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474

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