

Ambient Gas-Particle Partitioning of Tracers for Biogenic Oxidation

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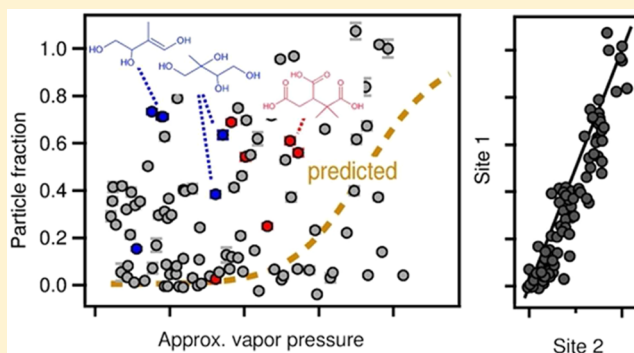
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Supporting Information

ABSTRACT: Exchange of atmospheric organic compounds between gas and particle phases is important in the production and chemistry of particle-phase mass but is poorly understood due to a lack of simultaneous measurements in both phases of individual compounds. Measurements of particle- and gas-phase organic compounds are reported here for the southeastern United States and central Amazonia. Polyols formed from isoprene oxidation contribute 8% and 15% on average to particle-phase organic mass at these sites but are also observed to have substantial gas-phase concentrations contrary to many models that treat these compounds as nonvolatile. The results of the present study show that the gas-particle partitioning of approximately 100 known and newly observed oxidation products is not well explained by environmental factors (e.g., temperature). Compounds having high vapor pressures have higher particle fractions than expected from absorptive equilibrium partitioning models. These observations support the conclusion that many commonly measured biogenic oxidation products may be bound in low-volatility mass (e.g., accretion products, inorganic-organic adducts) that decomposes to individual compounds on analysis. However, the nature and extent of any such bonding remains uncertain. Similar conclusions are reached for both study locations, and average particle fractions for a given compound are consistent within ~25% across measurement sites.



INTRODUCTION

Most reactive carbon emitted globally to the atmosphere is biogenic, consisting predominately of isoprene, followed by monoterpenes, and other terpenoid compounds.¹ Reactions of these gas-phase species with atmospheric oxidants can yield lower-volatility oxygenated products that partition to the particle phase, increasing the mass concentration of organic

aerosol ("OA", all discussion in this work limited to submicron particles)^{2–4} through the formation of oxidized secondary

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organic aerosol (SOA).⁵ While health and climate impacts of atmospheric organic carbon are primarily associated with particle-phase mass,³ organic aerosol is a dynamic, multiphase system⁶ that undergoes oxidation reactions both within and between the gas and particle phases that can yield both higher and lower volatility products.

Many compounds have been identified in ambient and laboratory studies that provide insight into the production of organic aerosol mass, but observations of actual ambient gas-particle partitioning are sparse. The volatility of organic species in the matrix of the ambient particle population is consequently uncertain, though it is critical for understanding the lifecycle of organic aerosol in the atmosphere.^{7–10} In many models, SOA is treated as semivolatile, meaning that molecular constituents partition between the gas and particle phases. Thermodynamic equilibrium is often used to model the extent of absorption into the particle phase and hence the organic mass concentration, which is primarily treated as a function of compound vapor pressure and total OA mass.^{6,11} This “organic absorptive equilibrium partitioning model” is often extended to individual monoterpene oxidation products (e.g., pinic acid) and for binned isoprene and monoterpene oxidation products.¹² In the case of isoprene photooxidation, which is a dominant process over the study areas described herein, chemically explicit models often treat individual identified particle-phase products and surrogate species to be essentially nonvolatile, formed after heterogeneous uptake of their precursor and not revolatilized.^{13,14} This assumption is reasonable for species having low expected vapor pressures such as organosulfates and multi-component esters and ethers (dimers, hetero-oligomers, etc.), which are thought to comprise a significant fraction of isoprene SOA.^{15–17} However, most compounds used to quantify isoprene-derived particle-phase mass (primarily C₅ polyols, e.g., ref 18) have estimated vapor pressures high enough to have a substantial or majority gas-phase component under typical atmospheric conditions and organic aerosol concentrations, supported by recent measurements of gas-phase 2-methyltetrols in a relatively dry environment.¹⁹ They may be sufficiently soluble in water, however, to remain largely in the particle-phase in humid environments, but solubility parameters are also often highly uncertain. While organic absorptive equilibrium partitioning has been widely used to effectively parametrize OA mass concentrations produced in chamber studies, recent ambient measurements have found that some organic compounds are well described while others are not.²⁰ Neither an assumption of nonvolatility for compounds of relatively high vapor pressures, nor an assumption of absorptive equilibrium partitioning of individual compounds has been extensively validated through observation of ambient aerosols.

Several additional processes have also been proposed to strongly influence gas-particle partitioning and in some cases better explain laboratory data, such as particle phase transport limitations,^{21,22} influence of inorganic ions on solubility,²³ and oligomerization reactions.²⁴ In particular, recent measurements of ambient particles have demonstrated the likely importance of oligomers¹⁵ and low-volatility products of accretion reactions that can thermally decompose to form fragments with the same formulas as many biogenic oxidation products.²⁵ Modeling of gas-particle partitioning has improved in recent years through the inclusion of kinetics and particle-phase reactions,^{26,27} and some work has suggested that accounting for these processes reconciles observed and expected partitioning.²⁵ However, a complete model treatment of organic absorption including

these processes remains elusive due to uncertainties in both model parameters and OA composition.

We present here measurements of fraction in the particle phase (F_p) of several compounds commonly used as “tracers” for the oxidation of biogenic volatile organic compounds (BVOC), as well as many newly measured compounds. Tracers uniquely identified by structure, mass spectrum, and/or chromatographic retention times are used to constrain the impact of known precursors or chemical pathways on the formation and removal of SOA. Decomposition of thermally labile low-volatility compounds may contribute to particle-phase concentrations of tracers,^{28–30} but the extent to which this process impacts tracer measurements is uncertain and must depend on the way the specific tracer is chemically bound in SOA. The practical consequence is that a “tracer” may represent a pure unambiguously identified compound or a pure compound plus mass from a converted analogue. This does not necessarily reduce its applicability as a tracer, but can increase the observed tendency of a tracer to stay in the particle phase and impact interpretation of tracer data. Ambient measurements of partitioning for tracers are consequently useful to understand the processes that drive exchange between gas and particle phases and to accurately include these transitions in chemically explicit models.

In this work, hourly concentrations of BVOC oxidation products in both the gas and particle phases were measured in two forested locations: the southeastern U.S. in rural Alabama during the summertime (“SOAS”) and central Amazonia (wet season: “IOP1”; dry season: “IOP2”) (details in ref 31). Previous measurements have shown that oxidation of isoprene and other biogenic emissions account for a major fraction of summertime particle-phase organic carbon in midlatitude forested regions such as the southeastern U.S. (e.g., ref 32 and refs therein), but few studies³³ have quantified BVOC oxidation products in the tropics. Consequently, though the bulk properties of the particles in the Amazon are well-studied,^{34,35} improved measurements of tracer compounds in the Amazon are needed to better understand the sources and atmospheric processing of organic compounds and study the processes controlling aerosol formation from biogenic emissions.

■ EXPERIMENTAL SECTION

This work is the result of measurements from several complex instruments at multiple field sites, compared to a number of different modeling approaches. All instruments, locations, and models are therefore described only briefly here, with greater detail in the [Supporting Information \(SI\)](#).

Partitioning and Concentration Measurements. Individual organic compounds were measured using a semi-volatile thermal desorption aerosol gas chromatograph (SV-TAG) with in situ derivatization,^{36,37} which provides hourly resolved concentrations and gas-particle partitioning of most common BVOC oxidation tracers (e.g., those measured by refs 32,38–40). Air is sampled at 10 Lpm through two identical cells containing a high-surface-area passivated metal-fiber filter that quantitatively collects gas- and particle-phase species less volatile than tetradecane.³⁷ Prior to collection, gas-phase mass is removed from one sample with a multichannel carbon denuder (MAST Carbon)—gas-particle partitioning is calculated as the ratio of these channels. Samples are desorbed with a ramped temperature (8 min: 30–310 °C, 35 °C/min) into helium saturated with a trimethylsilylation agent (“MSTFA,” N-

methyl-*N*-(trimethylsilyl) trifluoroacetamide) to a preconcentrating trap, which is then back-flushed and desorbed with a ramped temperature (3 min: 30–310 °C, held for 2 min) to a gas chromatography column for analysis by GC/MS (7890A/5975C, Agilent Technologies). Chromatography uses a non-polar column (Rtx-5Sil MS, 20 m × 0.18 mm × 0.18 μm; Restek) with a 23.6 °C/min temperature ramp (11.9 min: 50–330 °C). By ramping temperatures of high surface area components over several minutes, exposure of analytes to temperatures higher than necessary is minimized.

Compounds are quantified using isotopically labeled internal standards to correct for run-to-run variability in instrument response, and regular multipoint calibrations of approximately 100 authentic standards. Details and associated uncertainties of this approach are discussed in depth by Isaacman et al.³⁶ and provided in the SI; uncertainty is generally on the order of 20% of measurement.

SV-TAG measurements are validated wherever possible against known measurements and previously published results. Concentrations are compared with contemporaneous measurements based on traditional filter collection and extraction. Partitioning is compared to models for *n*-alkanoic acids, which have been shown previously²⁰ to be well-described by organic absorptive equilibrium partitioning (within the error uncertainty of SIMPOL vapor pressure estimation, approximately half an order of magnitude⁴¹).

Field Sites. Measurements were collected during three periods from two locations situated in rural areas where atmospheric composition is expected to be dominated by regional BVOC emissions and their oxidation products, with variable anthropogenic influence (map provided in Figure S1).

Data from the southeastern United States were collected from June 1 to July 15, 2013 as part of the Southern Oxidant and Aerosol Study (“SOAS”) at the Centreville, Alabama ground site (“CTR”; 32.90325 N, 87.24995 W; time zone: UTC-5). SV-TAG data are reported from June 4 to July 5, 2013, $[OA]_{\text{avg}} = 4.8 \text{ } \mu\text{g m}^{-3}$, $T_{\text{avg}} = 24.7 \text{ } ^\circ\text{C}$, $RH_{\text{avg}} = 82\%$. Samples were collected for 50 min every 1.5 h until June 18, and the first 22 min of each hour thereafter. The site is rural, primarily forested with a mixture of deciduous and coniferous trees. These measurements are referred to as “SOAS” or as “southeastern U.S.”

Data were collected in rural Brazil as part of the GoAmazon2014/5 field campaign,⁴² consisting of several ground sites and aircraft near Manaus, Brazil. Measurements presented in this work were made during the wet season (Intensive Operating Period 1, IOP1: February 1 to March 31, 2014) and the dry season (IOP2: August 15 to October 15, 2014) at the rural “T3” ground site (3.213 S, 60.599 W; time zone: UTC-4), 60 km west (downwind) of Manaus, with periods of strong anthropogenic influence from Manaus or regional biomass burning. SV-TAG data reported here span IOP1: February 14 to March 27, 2014, $[OA]_{\text{avg}} = 1.2 \text{ } \mu\text{g m}^{-3}$, $T_{\text{avg}} = 26.5 \text{ } ^\circ\text{C}$, $RH_{\text{avg}} = 90\%$, and IOP2: Aug 26 to Oct 4, 2014, $[OA]_{\text{avg}} = 8.7 \text{ } \mu\text{g m}^{-3}$, $T_{\text{avg}} = 27.9 \text{ } ^\circ\text{C}$, $RH_{\text{avg}} = 83\%$. Samples were collected during the first 22 min of every hour. These measurements are hereafter referred to as “GoAmazon2014/5 IOP1 or IOP2” or as “Amazon wet/dry season.”

Supporting Measurements and Models. Particle-phase mass and chemical composition (organic, sulfate, nitrate, ammonium, and chloride) were measured at both sites using an aerodyne high resolution time-of-flight aerosol mass spectrometer (“AMS”), which focuses particles through an

aerodynamic lens onto a 600 °C vaporizer for analysis using electron impact mass spectrometry.^{43–45} Temperature and relative humidity were measured at both sites with commercially available instrumentation. Gas-phase ammonia concentrations were measured at the SOAS CTR site, but not during GoAmazon2014/5. SV-TAG measurements were validated in part by comparison to filter samples collected at 1000 Lpm on quartz-fiber filters baked prior to sample collection at 550 °C. Samples were stored at −20 °C until extraction in methanol, trimethylsilylation, and analysis by GC/MS (5890/5971A, Hewlett-Packard).

Total particle-phase liquid water is calculated as the sum of water associated with inorganic ions and water associated with organic mass, assuming no interaction. The inorganic contribution is calculated using the thermodynamic model ISORROPIA-II,⁴⁶ shown previously to provide reasonable values at SOAS.^{47,48} Temperature, relative humidity, and AMS measurements of inorganic ions were used as inputs for modeling of both SOAS and IOP1. Gas-phase ammonia was included for SOAS but does not substantially impact calculated water concentrations (SI Figure S10). Water associated with organic mass is calculated based on the approach of Guo et al.,⁴⁸ using as inputs ambient relative humidity and the concentration and hygroscopicity of particle-phase organic mass measured by the AMS (SI eq S1). Hygroscopicity is estimated from the AMS oxygen-to-carbon ratios.⁴⁹

Observations of gas-particle partitioning are placed in the context of expected F_p using an organic absorptive equilibrium partitioning model that assumes instantaneous equilibrium between the gas and particle phases based on a compound’s vapor pressure (calculated using SIMPOL,⁴¹ a structure–activity relationship).^{11,50} Solubility in particle-phase liquid water is explored by expanding this model to assume equilibrium absorption into a mixed liquid phase composed of both organics and water, based on an empirically calculated effective partitioning coefficient. Phase separation of the particle is not considered here as estimated solubility parameters for the tracer compounds studied here are too uncertain to explicitly treat uptake into an aqueous phase (SI Figure S6 and Section S1.3.3). These models—absorptive equilibrium partitioning into pure organics or a mixed organic–aqueous phase—provide a baseline based on partitioning theory as it is often implemented in chemical transport models against which observations can be placed, as well as a framework for understanding the expected impact on partitioning of changes in meteorology and particle composition.

■ RESULTS AND DISCUSSION

Prevalence and Variability of Isoprene Oxidation Products. Products of isoprene (2-methyl-1,3-butadiene, C_5H_8) are of particular interest because this single species accounts for approximately half (600 TgC per year) of all nonmethane hydrocarbon emissions.¹ Laboratory studies of isoprene oxidation pathways expected in typical rural ambient environments have shown SOA formation to occur in large part through gas-phase formation of isoprene epoxydiol (IEPOX), followed by uptake into the particle and epoxide-opening reactions that yield polyols, oligomers, and organosulfates, among other possible products.^{51–54} Five of the most commonly measured tracers are reported here: two 2-methyltetrols (2-methylthreitol and 2-methylerythritol) and three isomers of methyl-trihydroxy-butene (“ C_5 alkene triols”).⁵⁵ These species are formed in the particle and, as

discussed above, most chemically explicit models do not include their revolatilization, but the data presented here demonstrate substantial concentrations of these tracers in both the gas- and particle-phase.

Isoprene oxidation products comprise a substantial fraction of SOA at both measurement locations (Figure 1a). In the

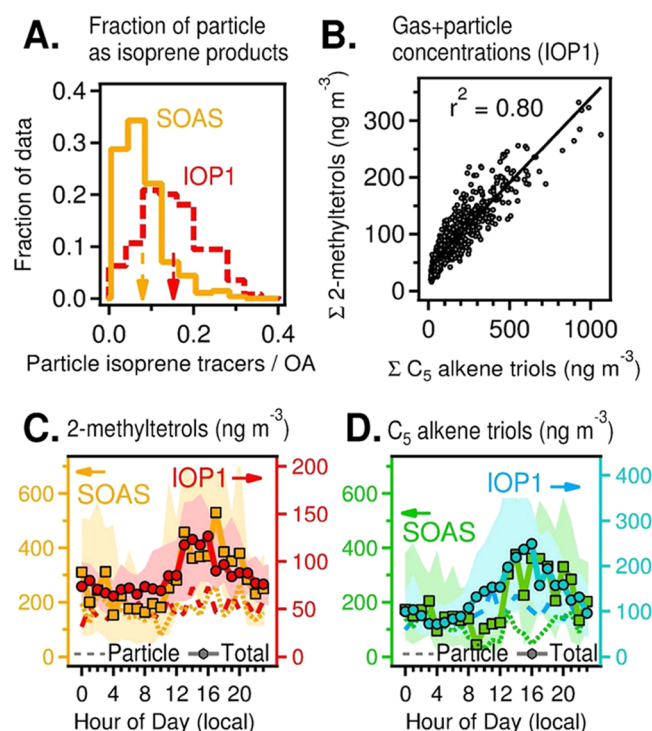


Figure 1. Concentrations and variability of concentrations of 2-methyltetrols and C_5 alkene triols. (A) Histogram of the fraction of total organic aerosol mass concentration (measured by an AMS) that is explained by the sum of these compounds (measured by SV-TAG) during measurements in the GoAmazon2014/5 IOP1 (red dashed) and SOAS (orange solid). Variability shown as (B) a comparison between total concentrations of these two compound classes, and diurnal concentrations (markers: gas plus particle, dashed: particle only) of (C) the sum of 2-methyltetrol isomers (red: Amazon wet season, orange: southeastern U.S.) and (D) the sum of C_5 alkene triol isomers (cyan: Amazon wet season, green: southeastern U.S.). Markers and lines are medians, shaded area is interquartile range. Panels (C) and (D) are expanded to provide detail in SI Figure S12.

summertime in rural Alabama, these five IEPOX-derived polyols account for on average 8.0% of all OA mass (with some periods up to ~20%), and approximately 15% of OA mass in the Amazonian wet season (up to ~35%), in reasonable agreement with contemporaneous and previous bulk measurements at both sites.^{34,48,56,57} The close correlation ($r^2 = 0.80$) of total gas plus particle phase concentrations of these two compound classes (Figure 1b, data from IOP1 shown as an example) suggests that, as expected, they are formed through similar chemical pathways.

Given their high concentrations, the dynamics, partitioning, and variability of these polyols serve as useful examples for the properties and chemistry of particle-phase organic mass. Total gas-plus-particle-phase isoprene oxidation products (Figure 1c,d) are maximum during the afternoon, approximately coincident with isoprene concentrations in both regions.^{35,47} Gas-phase concentrations increase in the afternoon, while the

daily cycle in particle-phase concentrations is weaker (GoAmazon2014/5) or absent (SOAS). Though the correlation between total concentrations of these compound classes supports a shared or related formation mechanism (e.g., particle-phase reactions of IEPOX), the presence of a large but variable gas-phase component indicates that either partitioning to the gas-phase occurs following in-particle formation of these compounds, or gas-phase formation of these species are more important formation pathways than typically considered in models. In either case, a large gas-phase component must be considered in understanding these tracers.

Diurnal trends in concentrations result in an average afternoon minimum in the fraction of each compound that is in the particle (Figure 2a,b), F_p . However, changes in F_p of these two compound classes do not have the same daily pattern, with a sharper valley in the partitioning of C_5 alkene triols around 1600 (local) at both sites. Furthermore, while 2-methyltetrols have a similar or smaller fraction in the particle phase in the Amazon wet season than at the SOAS site, the opposite is true for C_5 alkene triols. In general, IOP1 has lower particle-phase organic mass and higher temperatures, though SOAS exhibits stronger diurnal changes in temperature; diurnal profiles of these environmental conditions are provided in SI Figure S11. Observed F_p is closely correlated for isomers (e.g., 2-methylthreitol vs 2-methylerythritol, $r^2 = 0.86$, shown in SI Figure S14). However, despite similar average F_p and qualitative diurnal trends, observed partitioning of the tetrols is in fact poorly correlated with partitioning of the triols (Figure 2c). This conclusion qualitatively extends beyond isoprene products to α -pinene oxidation products, which also have poorly correlated partitioning ($r^2 < 0.2$) even for compounds with similar average F_p and functional groups (examples shown in SI Figure S17). A model in which variability of tracer partitioning is driven primarily by external conditions (e.g., temperature or particle composition) without consideration for compound functionality or identity is therefore insufficient to describe the observations. Instead, observed partitioning appears to be driven in large part by compound-specific processes that are not clear in typical measurements of these species (e.g., accretion reactions, association with inorganic ions, compound-dependent temperature sensitivity of vapor pressure, etc.), or by physical processes that are independent of vapor pressure (e.g., in-particle diffusion).

Factors Influencing Partitioning of Individual Tracers.

Observations of polyol partitioning are in fact found to be poorly described by either an absorptive equilibrium partitioning model, as expected from the discussion above, or by assumptions of nonvolatility. The histogram of observed partitioning for these tracers (2-methylerythritol shown as a representative example in Figure 2d) demonstrates that F_p is highly variable, ranging from all mass in the particle-phase to nearly all mass in the gas-phase; on average it is approximately evenly split between phases. These data do not support an assumption of nonvolatility. However, F_p is also substantially higher than expected based on vapor pressure (Figure 2d, black solid line) and correlation with an organic absorptive partitioning model is poor ($r^2 = 0.14$); vapor pressure is calculated for each sample at the measured ambient temperature using SIMPOL. High F_p is not due simply to bias in the model from overestimation of vapor pressure of this species or poor prediction of partitioning coefficients; the dashed line Figure 2d shows the results of the absorptive equilibrium partitioning model in which an empirical uptake parameter

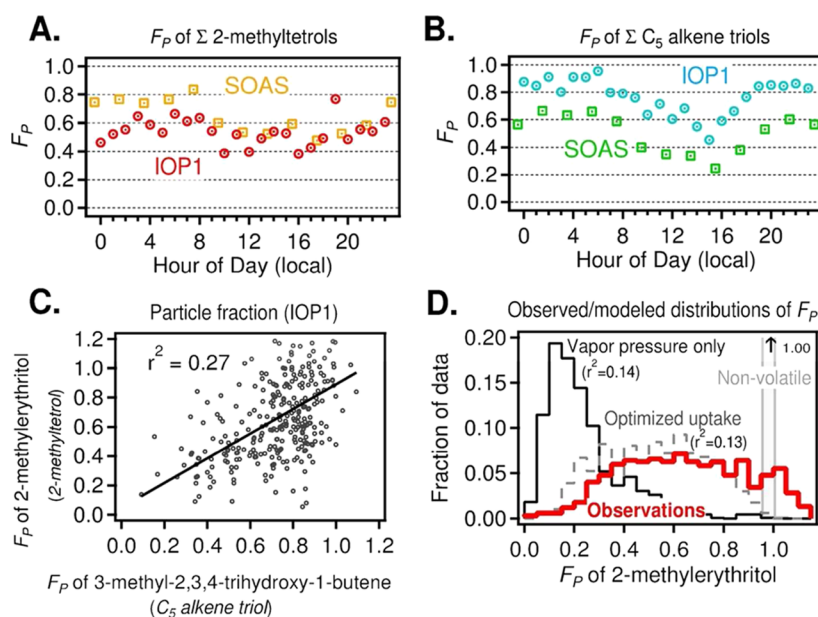


Figure 2. Observations and variability of F_p of 2-methyltetrols and C_5 alkene triols. Diurnal profiles of F_p of (A) the sum of 2-methyltetrol isomers (red: Amazon wet season, orange: southeastern U.S.) and (B) the sum of C_5 alkene triol isomers (cyan: Amazon wet season, green: southeastern U.S.) and (C) comparison of F_p during the Amazon wet season of one isomer in each class measurements. (D) Distributions of observations and models shown as histograms of observed F_p (red line) for a representative polyol, 2-methylerythritol, and predictions based on several common atmospheric partitioning modeling frameworks for this compound: assumed nonvolatility (gray bar), organic absorptive equilibrium partitioning (black line), and absorptive equilibrium partitioning (dashed gray line) into a combined organic and aqueous phase with an uptake parameter that minimizes bias from the observations. Correlation between model and observations are provided in parentheses.

(e.g., vapor pressure) is optimized to minimize the average difference between the observed and expected F_p (i.e., the slope of the fit) with no a priori assumptions about volatility or solubility. This optimized equilibrium model necessarily better estimates average F_p but is no better at predicting temporal variability ($r^2 = 0.13$), whether solubility in particle-phase liquid water is included (as shown in Figure 2d, with the inclusion of solubility described in the SI), or whether only absorption into organic mass is considered as in the case of the organic absorptive equilibrium partitioning model (both correlations shown in SI Figure S7b,c). Changing the temperature dependence of the vapor pressure also does not improve its ability to capture temporal variability. While these models do exhibit some skill in predicting F_p of some compounds (e.g., pinic acid, shown in SI Figure S16 and ref 20), variability of observed partitioning for many individually measured tracers is not easily explained by current widely used atmospheric modeling frameworks.

It should be noted that many details of equilibrium absorption are still uncertain and, as such, are simplified in the models tested here. Time-independent factors (e.g., biases in vapor pressure) likely do not contribute substantially to the observed differences, as they would be compensated for by the optimization of the uptake parameter (dashed line, Figure 2d). However, time- (or composition-) dependent changes to equilibrium partitioning parameters cannot be excluded. In many implementations (though not all, e.g., refs 58 and 59), organic absorptive equilibrium partitioning models assume ideal conditions (an activity coefficient of unity) despite expected dependence on compound functionality, particle phase state, and organic composition.⁶⁰ Some compounds discussed here have chemical properties (e.g., oxygen to carbon ratio, solubility, etc.) similar to the bulk organic particle composition. For such compounds strong barriers to partitioning are not

expected for organic absorptive equilibrium partitioning and an assumption of approximate ideality is not unreasonable, but even in these cases time-dependent variation in activity cannot be discounted as a factor and nonideal aqueous uptake may impact partitioning. A comprehensive implementation of absorptive equilibrium partitioning with compound-dependent and temporally variable activity coefficients may better describe the observations, but the complexity of organic composition and the uncertainty in relevant parameters create barriers to any such comprehensive implementation.

Several factors impacting ambient observations may contribute to real complexity that require greater understanding of atmospheric composition and chemistry, not only improved implementation of absorptive equilibrium partitioning models. These include complex bonding in particle-phase organic compounds that result in poorly characterized organic mass (e.g., the presence of low-volatility compounds that decompose during analysis), physical limitations that impede equilibrium on the time scales of formation and measurement, or dissolution processes that are not captured by an assumption of instantaneous thermodynamic equilibrium with an aqueous phase. Diffusion limitations and high viscosity within the particle are not likely as the particles are expected to be liquid at most times, which has been demonstrated for GoAmazon2014/5.⁶¹ Solubility of organic species in pure particle-phase liquid water may, like absorption into an organic phase, occur at approximate thermodynamic equilibrium. Consequently the inability of the optimized equilibrium absorption model to capture observed variability in F_p , as well as poorly correlated F_p for chemically similar compounds, suggests that unmediated solubility is unlikely to dominate partitioning for most observed species. However, there are complex uptake processes (e.g., solvation mediated by inorganic ions) that cannot be discounted but are not yet sufficiently understood to be

comprehensively implemented in models. The high fraction in the particle of these tracers might therefore be explained by recent work suggesting that biogenic oxidation products exist in large fraction as low-volatility products that can thermally decompose to form constituent higher volatility components.²⁵ The tracers measured in this work represent many compounds traditionally included in chemically explicit models, so these data provide a crucial step toward reconciling our traditional understanding of the components of biogenic SOA—most of which have relatively high vapor pressures—with bulk measurements, which often find ambient SOA to have relatively low volatility.²¹

Assuming relatively minor influence of dissolution and particle viscosity on observed partitioning, contribution to particle-phase tracer concentrations by low-volatility mass can be roughly estimated as the difference between observed F_p and that estimated from vapor pressure. Error on vapor pressure is estimated at approximately half an order of magnitude, so this approach is imprecise, but it is nevertheless a useful means to explore the potential ubiquity of these low-volatility products. On average half of particle-phase 2-methylerythritol mass in the southeastern U.S. is unexplained by vapor pressure of the pure species, and nearly three-quarters during the Amazon wet season. While this analysis provides some insight, quantitative understanding of low-volatility content of these tracer species assumes that absorptive equilibrium partitioning models based on vapor pressure are sufficient to describe partitioning of the pure species of these tracer compounds. There is some recent evidence for this assumption,²⁵ but it has not yet been tested in a diversity of environments and does not include the potentially important impact of processes that may slow time scales to reach equilibrium (e.g., kinetically limited reactions), or are poorly understood modifiers on that equilibrium (e.g., formation of inorganic adducts, composition-dependent activity coefficients). Furthermore, the high particle-phase liquid water content during these campaigns may increase partitioning to the particle phase,^{58,62} but quantitative estimation of this effect is impeded by large uncertainties in solubility and activity parameters. Consequently, the estimate of low-volatility content provided here is qualitative. However, this inferred fraction of low-volatility mass is substantially higher than measurement differences between SV-TAG and colocated filter-based measurement techniques (SI Figure S3), suggesting potential widespread measurement of low-volatility mass as pure discrete tracer species across measurement platforms.

The observed high F_p values for these tracers, coupled with recent observations of low-volatility accretion products raises significant questions about the nature of the bonds keeping these tracers in the particle phase. Many classes of low-volatility compounds have been observed in ambient particle samples, but most of these cannot easily explain the observed tracer F_p results. Thermal decomposition of organosulfates, for instance, was found in laboratory tests of SV-TAG to negligibly contribute to measured mass (<5% conversion to analogous species). Similarly, dimers and other oligomers have been shown to survive gas and liquid chromatographic analysis techniques^{53,39,63,64} but are nevertheless not commonly observed at high concentrations in ambient environments by these techniques.⁶⁵ Consequently, any low-volatility particle-phase mass that yields these tracers upon thermal decomposition is poorly characterized and potentially comprised of (a) these discrete low-volatility compounds formed directly through oxidation processes (though for the reasons described

above this is least likely), (b) macromolecules composed of many covalently bonded monomeric units formed through oligomerization or other accretion reactions,^{66–68} and/or (c) inorganic–organic adducts. The presence of a high-molecular-weight component of organic aerosol has been widely observed using laboratory based analysis techniques,^{69,70} supporting interpretation (b) that some fraction of tracer mass may be bound in large, low-volatility macromolecules. However, improved chemical and structural understanding of particle-phase mass, low-volatility content, and its transformation processes, is still needed to accurately implement traditional partitioning models for individual tracers and confirm whether or not equilibrium partitioning can be reasonably applied to the pure or monomeric fraction of these tracers under ambient conditions. This points to a continued need for new measurement techniques that can identify, chemically characterize, and quantify tracers in both their pure form and any potentially labile products.

F_p of Biogenic Oxidation Products. The general trends observed for isoprene products are found in our data to extend to most observed biogenic oxidation products. The diurnal variability in F_p observed for polyols—a change of 20–40% between night and day—is exhibited (Figure 3) not just for the

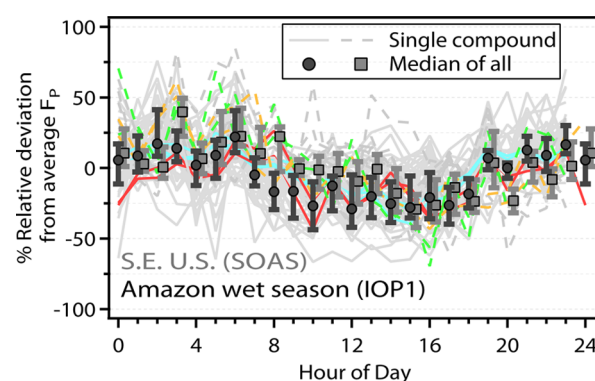


Figure 3. Median diurnal variability in F_p for all observed partitioned (average $0.1 < F_p < 0.9$) compounds. Points are medians of all compounds, vertical bars are interquartile range (dark circles: Amazon wet season, light squares: southeastern U.S.). Median diurnal of each compound shown as a line, including those shown in other panels (lines of same colors) and all other observed partitioned compounds (gray) (GoAmazon2014 IOP1: solid lines, $N = 44$; SOAS: dashed lines, $N = 16$).

isoprene tracers but also for nearly all observed partitioned compounds (operationally defined here as $0.1 < F_p < 0.9$). This is qualitatively similar to expectations from absorptive equilibrium partitioning models (lower F_p during the warmer hours of the day). However, the variability in environmental factors predicts a trend that is temporally shifted and in most cases stronger than observed (provided in SI Figure S13), supporting the conclusion that while there is a tendency of these systems toward thermodynamic equilibrium, compound-specific reactions and bonding have a substantial influence observed gas-particle partitioning.

The average F_p of 103 oxygenated compounds observed in the Amazon wet season is shown in Figure 4a relative to chromatographic retention time, which is strongly correlated with vapor pressure (SI Figure S5). Though a few of these compounds are known tracers for biogenic oxidation (labeled with letters), most have no matching mass spectra in the

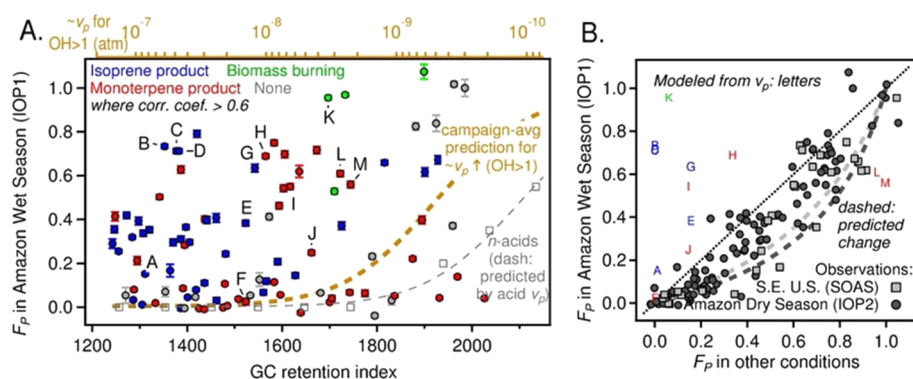


Figure 4. Campaign average ($\pm$ standard error) of observed F_p in the Amazon wet season (IOP1). Shown as (A) a function of chromatographic retention time, a proxy for vapor pressure. Known compounds labeled as letters (identified in SI Table S4–7), and unknown compounds colored by correlation to known (gray for $r < 0.6$). Vapor pressure for compounds with more than one OH group (estimated from SI eq S6) shown on orange axis, with campaign-average F_p expected assuming thermodynamic equilibrium with organic mass shown (dashed orange line). Observed F_p of n -alkanoic acids (gray squares) from one period (“Event 2” in SI Figure S4) shown for reference, with the same thermodynamic equilibrium model (dashed gray line) applied for this time period. Average IOP1 observations compared in (B) to average F_p at SOAS (light squares), IOP2 (dark circles), and expected F_p modeled from vapor pressure using the same framework (letters). Dashed lines represent the expected change in average F_p between campaigns from changes in particle composition, modeled assuming absorption into both organic and aqueous mass (SI eq S14).

scientific literature. Almost all correlate well with known tracers (provided in SI Table S7) and can serve as unidentified tracers for biogenic oxidation, subject to the same considerations as known tracers in interpreting results.

Observed average F_p does not correlate with the vapor pressure calculated from retention time, and individually measured compounds tend to exist largely in the particle phase despite relatively high vapor pressures. The expected F_p based on the organic absorptive equilibrium partitioning model (dashed orange line) provides a rough expectation of partitioning in this environment and its trend with retention time. To validate measurements, F_p of C_{12-23} n -alkanoic acids is shown (dashed gray line) for a short period when they are consistently above levels of detection to demonstrate that, as previously reported,²⁰ they are found to agree with an organic absorptive equilibrium partitioning model of this time period (four such time periods shown in SI Figure S4). In contrast to n -alkanoic acids, no strong correlation is observed between F_p of these biogenic oxidation tracers and their elution order. Most observed compounds have a higher-than-expected average measured F_p . However, very few of the observed compounds can be reasonably assumed to be nonvolatile. Instead, a substantial majority of observed tracers can be best represented as partitioning between the gas and particle phases, with a nighttime high and daytime low in F_p .

Our ability to confidently model partitioning of tracers is hindered by the observed lack of correlation with vapor pressure or environmental factors, and the difficulty in knowing the fraction and identity of low-volatility mass contributing to measurements. However, comparison of observations from each measurement period provides constraints on the variability of F_p and the influence of these factors between environments. Despite differences in particle composition and meteorology, the average fraction of a given compound in the particle is similar between measurement periods and sites (Figure 4b). Although large temporal variability exists for F_p of most compounds (often with a range of up to 1.0), average daytime F_p for most compounds varies by less than 25% between the measurement periods, with the wet season (IOP1, left axis) having a lower F_p than the dry season or SOAS (bottom axis). In general, observed changes in average F_p between measure-

ment periods were substantially smaller than shifts in expected equilibrium caused by changes in OA mass concentration, temperature, and particle-phase liquid water (dashed lines in Figure 4b), whether or not water solubility is included (both cases shown in SI Figure S19). Most of these species, at least in their measured form, cannot therefore be well described by changes in external conditions. However, the chemistry at each site is apparently sufficient similar to drive only small changes in average partitioning. It is important to note, though, that there is substantial heterogeneity among species; for example, some tracers (e.g., pinic acid) are indeed reasonably well described by organic absorptive equilibrium partitioning, highlighting the need for continued investigation of these processes. The observations from these measurement sites, provided in SI Table S4, can serve as a reasonable proxy for average F_p of tracer compounds under similar conditions. Effective empirical uptake parameters used to estimate expected changes (dashed lines) between measurement periods are also provided in the SI (Tables S5, S6) for use in future work.

Atmospheric Implications. Nearly all SV-TAG observed compounds are partitioned between the gas and particle phases, and the particle fractions of individual compounds observed in this work do not exhibit the expected relationships between volatility, pure vapor pressure and particle composition expected from absorptive equilibrium partitioning relationships. Many tracers and individually measured compounds instead exhibit trends that suggest they are chemically bound to the particle. However, the nature of these bonds is uncertain, and may include a combination of traditionally considered low-volatility products such as oligomers that can thermally decompose, larger and more complex accretion products containing many different monomeric units (i.e., macromolecules), and association with inorganic ions—all of which have been observed in previous work. This does not necessarily dispute the use of absorptive equilibrium partitioning to parametrize bulk SOA properties. Instead, these data suggest that when considering the real-world partitioning of an individual compound, absorptive equilibrium partitioning models are challenged by poor chemical understanding of decomposable mass, current instrument limitations, and uncertainty in model parameters. Future characterization of

low-volatility particle-phase mass may improve the application of these models to tracers by coupling thermodynamic partitioning of pure discrete components with a better understanding of the bonds that increase their apparent F_p , and other potentially important kinetically limited processes.

The observed tendency of tracers to exhibit relatively consistent average F_p between measurement sites provides a substantial step toward accurately modeling the fate of BVOC-derived SOA. The average measurements of F_p made here can be used as approximate tracer partitioning parameters in current models and measurements while work continues to parametrize all relevant nonequilibrium processes and to fully understand the influence and identity of low-volatility mass. Owing to the observed diurnal variability, both daytime and nighttime values are provided in the SI (Table S4) for future application. These data also suggest in part that current literature values for formation rates and concentrations of these tracer molecules should be considered effective measurements of both tracer molecule and some thermally labile low-volatility constituent. This may help explain observations²¹ of low-volatility bulk OA mass despite high concentrations of tracers with high vapor pressure.

While F_p of measured tracers is generally higher than expected based on vapor pressure of the pure tracer species, most species are observed to have a significant gas-phase component. Measurement of 2-methyltetrols and C_5 alkene triols in the gas-phase provides evidence of the importance of chemical mechanisms that are not considered in most chemically explicit treatments of isoprene oxidation: volatilization of these oxidation products from the particle and/or significant formation of these products in the gas phase. Consequently, gas-phase loss processes, including oxidation reactions as well as efficient deposition of highly oxidized gases to the surface,⁷¹ need to be considered in the lifecycle of these and other organic aerosol components. This conclusion has significant implications for tracer-based source apportionment and understanding the fate of BVOC-derived OA, which comprise a large fraction of submicron atmospheric particulate mass.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01674.

Details on instrument operation and capabilities, descriptions of measurement locations, and discussion of models used in this work is provided in the Supporting Information. This information includes results impacting the interpretation and use of these data (e.g., model outputs, instrument validation, etc.) Additional detail is also provided on some results, including further exploration of partitioning correlations between compounds and sites, and tables providing average partitioning parameters for all observed compounds (data used in Figure 4) (PDF)

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The authors declare no competing financial interest.

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