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Secondary organic aerosol contributes to the atmospheric particle burden with implications for air quality and climate. Biogenic volatile organic compounds emitted from plants are important secondary organic aerosol precursors with isoprene emissions dominating globally. However, its yield of particle mass from oxidation is generally modest compared to that of other terpenoids. Here we show that isoprene, carbon monoxide and methane can suppress the instantaneous mass and the overall mass yield derived from monoterpenes in mixtures. We find that isoprene scavenges hydroxyl radicals preventing reaction with monoterpenes and the resulting isoprene peroxy radicals scavenge highly oxygenated monoterpene products. These effects reduced the yield of low-volatility products that would otherwise form secondary organic aerosol. Global model calculations indicate that oxidant and product scavenging can operate effectively in the real atmosphere. Highly reactive, modest aerosol yield compounds are not necessarily net producers and their oxidation can suppress both particle number and mass.

Introduction

The secondary organic fraction of fine aerosol is substantial[1,2] and contributes significantly to the fine particulate matter (PM) burden[3] and aerosol impacts on climate[4]. Conventionally, Secondary Organic Aerosol (SOA) particle mass is considered to be formed independently from the condensable oxidation products of each contributing volatile organic compound (VOC)[5]. The ambient atmosphere is a complex mixture of biogenic and anthropogenic VOC, a limited number of which are normally considered to control the oxidant concentrations in air quality or climate models[4,5]. Isoprene has been found to dominate plant VOC emissions globally[6,7], though it has been found only moderately effective at forming SOA particle mass[8,9,10]. Nevertheless, isoprene oxidation tracers have been observed in particles in both chamber experiments[11,12] and the atmosphere[11,13,14,15] showing that they condense from the gas phase. Oxidation of the monoterpenes (MT), including α-pinene, and sesquiterpenes is generally more efficient at producing SOA particle mass[16,17,18]. When oxidation of a VOC contributing to SOA is explicitly considered in models, some interaction between the oxidant field and the SOA formation process is implicit[5], though recently observed behaviour is yet to be described. Two such recent findings have motivated the current work. First, it has been shown that C_5 isoprene molecules suppress the nucleation of SOA particles in the oxidation of the C_{10} MT in mixtures of plant emissions by successfully competing for the hydroxyl radical, OH[19,20,21]. Second, recent direct observation of highly oxygenated organic molecules (HOM) formed from MT oxidation[22], and elucidation of the auto-oxidation mechanisms by which they are formed, have implicated them in the formation of new SOA particles. Our work moves beyond the suppression of particle nucleation by isoprene using the new mechanistic understanding to explain SOA mass and yield suppression in MT-containing mixtures. These results highlight a need for more realistic consideration of SOA formation in the atmosphere analogous to the treatment of ozone formation, where interactions between the mechanistic pathways involving peroxy radicals are recognised to be essential[23].

Use of SOA yields in mixtures

Ostensibly, the concept of a SOA yield is straightforward and unambiguous[24-26]. It has been widely used to interpret the potential of precursor molecules to produce particulate mass, most extensively from smog chamber studies and usually with the goal of quantifying the formation of ambient atmospheric particles. Yield is normally defined in terms of the particulate mass condensed for a given mass of gaseous parent VOC consumed. The process of determining SOA yields presents substantial practical challenges. Notwithstanding measurement uncertainties and artefacts (for example, wall losses and those associated with the accurate determination of the mass of semi-volatile material[27-31]) there are numerous reasons why SOA yields may vary according to the conditions under which they are measured. This paper does not aim to provide a critical evaluation of the determination of SOA yields and their extrapolation to atmospheric conditions and the reader is referred to a number of recent publications for a discussion of challenges and the state-of-the-science concerning the interpretation of SOA formation from chamber experiments[22,27,29-32]. However, there are conceptual aspects often implicit in the treatment of SOA formation either in chamber experiments, real atmospheric mixtures, or models of the atmosphere that provide the context for the current study.

First, the concept of yield frequently includes some assumption of equilibrium. An interpretation of particle mass in terms of the partitioning of components of known volatility by absorptive partitioning invokes an equilibrium assumption. In reality, mass takes a finite time to transfer between the continuous and dispersed phases[33,34]. Second, a parent VOC will continue to react, as will its reaction products, provided they have reaction partners. Under atmospheric, or simulated atmospheric, conditions the reaction partners are normally oxidants, such as the hydroxyl radical OH (the main focus in this paper). This means that the distribution of vapour phase components that is available to transfer to the condensed phase by condensational growth or nucleation is continuously evolving through photochemical reactions. Third, a yield integrates across all oxidation products formed from the parent hydrocarbon, summing the fraction of these products that will partition to the particle phase from whatever stage of oxidation under the chosen reaction conditions. We further would like to note that the yields themselves can be dependent on the oxidant concentration[e.g.31,32].

This combination of characteristics raises first order challenges when considering SOA formation in the real atmosphere which comprises a complex mixture of organic vapours of widely varying volatilities, from numerous sources of anthropogenic and biogenic origin. This paper is concerned with the challenge surrounding the introduction of oxidants into the atmospheric mixture and the reactivity of the evolving components in the mixture – specifically, the yield of condensed organic particulate material of any of the single component vapours in the mixture when it is consumed by the oxidant. Any of the vapours may react with the available oxidant, so from the perspective of any other vapour molecule, the oxidant has been "scavenged" and is unavailable as a reaction partner. Our experimental systems illustrate the implications on SOA formation of mixtures of precursors. We demonstrate how SOA yield in mixtures is dependent on whether the reactivity of one of the SOA forming compounds controls the oxidant and contrast conditions in the laboratory and the atmosphere. It is not only the oxidants that can be removed from the system by components of a mixture. The products from oxidation that can react to form the final condensable SOA precursors may alternatively be scavenged by other reactive

139 intermediates. This process can form the basis for the reduction in yield of the
140 individual components in a mixture, as shown by our results below and detailed in the
141 supplement sections.

142

143 **Experiments to SOA formation in mixtures**

144 In the Jülich Plant Atmosphere Chamber (JPAC; suppl. section 1) we find that the
145 presence of isoprene substantially suppresses the SOA mass formed from oxidation of
146 α-pinene, the most abundant MT in the atmosphere (Figure 1A). Furthermore, we
147 show that this reduction of SOA mass is not trivially due to the lower amount of MT
148 consumed in the presence of isoprene. Rather the presence of isoprene actually
149 suppresses the SOA mass yield from the amount of VOC consumed (Figure 1B).
150 Isoprene thereby limits not only new particle formation[19] (hence exhibiting control
151 over particle number concentration) but also the growth of pre-existing particles and
152 thus their size. This has significant consequences for the abundance of PM mass
153 formed in the mixture and the number of particles that may grow to sizes where they
154 can act as cloud seeds. Our findings are surprising and unexpected in the context of
155 existing conceptions of SOA mass yields (suppl. section 2). As shown in Figure 1, the
156 presence of isoprene substantially suppresses the SOA mass formation from α-pinene
157 oxidation by about 60% and the SOA yield by 40%. Figure S2 shows even greater
158 suppression in greater isoprene excess, with both mass and yield reduced in the
159 presence of both neutral and acidic seed. This contrasts sharply with current
160 understanding, since isoprene oxidation should contribute substantially to SOA
161 production when isoprene concentrations are high.

162 Below we describe the two effects contributing to SOA suppression - oxidant
163 scavenging and product scavenging. This demonstrates the importance of accounting
164 for the reactivity of the parent VOC in atmospheric mixtures and hence their turnover
165 (suppl. section 2) as well as interactions between their reaction intermediates and
166 products. Whilst our experiments illustrate this requirement predominantly with
167 reference to the photochemical isoprene – α-pinene system with OH as the major
168 oxidant, it should be noted that in all mixed systems investigated, OH (oxidant)
169 scavenging and product scavenging were found to reduce both the SOA particle mass
170 and the SOA yield. Note that during daytime, both, ozonolysis and OH oxidation of
171 α-pinene, contribute to SOA, as in our experiments, however the contribution via OH
172 reactions here was much greater than 90%. According to our mechanistic
173 understanding presented below, product scavenging will be similarly effective for OH
174 and O_3 oxidation.

175

176 **Oxidant and product scavenging**

177 Oxidant scavenging is demonstrated by the decrease in SOA mass and yield of the
178 mixture with increasing isoprene fraction as well as by the decrease of the α-pinene
179 yield itself (Figure 1B and suppl. section 3). The contribution of isoprene to SOA
180 mass in the presence of neutral ammonium sulfate aerosols is small and α-pinene
181 oxidation products make up the overwhelming fraction of SOA in mixtures. Isoprene
182 increasingly efficiently competes with α-pinene for the available OH as the reaction
183 system is stepped from high SOA yield pure α-pinene to low SOA yield pure isoprene
184 (Figure S2). With respect to α-pinene, the isoprene "scavenges" the OH[19], i.e. the
185 steady state OH concentration is lowered by the introduction of isoprene for a given

186 OH source strength, therefore less OH can react with α-pinene, resulting in less SOA
187 mass being formed. In addition, the SOA yield itself is dependent on [OH][31,32].
188 By uniquely being able to control the OH at the same concentration with and without
189 isoprene addition by readjusting its source strength, we were able to reveal that the
190 SOA mass (Figure 1A), and by implication the α-pinene SOA yield (Figure 1B, 3rd
191 bar), decreased with increasing isoprene in the mixture (suppl. section 4). Strikingly,
192 the α-pinene SOA yield was reduced by 30% relative to the pure α-pinene yield, even
193 though the OH scavenging effect has been removed (Δisoprene/Δα-pinene≈1±0.2
194 [ppb/ppb] = 0.5±0.1 [μg/μg]). Moreover, by re-adjusting [OH], we held the α-pinene
195 sub-system of the mixture at the same stage of oxidation as in the pure case. This
196 results in the condensing oxidation products having the same "chemical age" in both
197 cases, thereby avoiding comparison of chemical systems of different chemical
198 evolution.
199 In Figure 2 we show the actual α-pinene SOA yields (y_{act}) in the mixture normalized
200 to the α-pinene SOA yield y_{AP} = 17% for pure α-pinene in absence of isoprene. The
201 y_{act} were calculated from the observed SOA mass and the actual consumption of α-
202 pinene. Depending on the isoprene to α-pinene ratio, SOA mass produced from the
203 same amount of consumed α-pinene in the presence of isoprene can be reduced by
204 more than half compared to the amount formed when oxidised alone (Figure 2).
205 Clearly, smaller amounts of SOA forming products from α-pinene oxidation are
206 formed in the presence of isoprene – we denote this effect "product scavenging" .
207 The product scavenging effect (and the OH scavenging effect) on SOA formation is
208 somewhat masked in the presence of the acidic seed aerosol with which isoprene has
209 a significant yield[12,35-37] (suppl. section 4, Figure S3, Figure 1B, 6th bar). Replacing
210 isoprene by CO shows, that the acidity of the seed particles did not affect the
211 behaviour of α-pinene (Figure S3), but indeed enhanced the isoprene contribution
212 (Figure S4). This underlines the importance of liquid phase processes for isoprene,
213 but also clearly shows that both scavenging effects are general phenomena in the gas
214 phase.
215 SOA yield suppression also occurs when isoprene is mixed with β-pinene and when
216 CO or CH_4 were mixed with α-pinene (suppl. section 5, Figures S5-S7, Figure 4).
217 This generality ensures that the influence of the relative reactivity of components in
218 mixtures on the SOA formation potential has much more profound implications than a
219 simple reduction in yield in each of the binary mixtures. Moreover, because of
220 potential interactions with additional SOA contributors, the yields in anything beyond
221 the binary mixtures cannot be simply added or in any way predicted without specific
222 mechanistic insight.
223 The key to a mechanistic understanding of the product scavenging is the formation of
224 HOM with the peculiarity that HOM peroxy radicals also dimerise in the gas phase[38]
225 (suppl. section 6). It can be inferred from their structure and O/C ratios that HOM and
226 even moreso their dimers, are low to extremely low volatility organic compounds[22,39]
227 and will contribute substantially to SOA formation and initial growth[22,39].
228 In Figure 3A we present direct observation of the product scavenging of α-pinene
229 HOM by comparing mass spectra measured in OH reaction systems for α-pinene-only
230 and for an α-pinene/isoprene mixture. For α-pinene-only we observed about equal
231 signal intensities in the ranges of α-pinene HOM monomers with 10 C-atoms and of
232 HOM dimers with 17-20 C-atoms. In the presence of isoprene, α-pinene dimers are
233 suppressed by a factor of about 3. Comparable dimer suppression by a factor of 2 is
234 observed for CO (Figure 4A). HOM dimers have been observed in the boreal ambient
235 atmosphere, lower during daytime than at night-time, but at lower fractions than in

236 our α-pinene-only experiments[40,41]. Since product scavenging will be occurring,
237 particularly during daytime, these observations are consistent with our findings.
238 The strength of product scavenging is estimated by comparing two sets of
239 experiments where the [OH] was tuned, either by varying the OH sink through adding
240 different amounts of isoprene to the reaction system or by varying the OH production
241 rate through modifying the photolysis rate $J(O^1D)$ for O_3 (Figure 3B). With increasing
242 isoprene, the dimers are more strongly suppressed than with decreasing $J(O^1D)$ as a
243 result of increased scavenging of α-pinene HOM peroxy radicals by isoprene related
244 RO_2 and HO_2 radicals[42]. This leads to formation of less HOM, mainly by diminishing
245 α-pinene HOM self-dimerization. Suppression of the HOM dimers alone accounts for
246 27% reduction in HOM mass (Figure 3C) and explains most of the 35% SOA mass
247 reduction by the product scavenging effect shown in Figure 1, underlining the pivotal
248 role of HOM dimers in new particle and SOA formation[22,39]. The involvement of
249 HOM does not preclude the involvement of multigenerational oxidation as such (cf.
250 suppl. section 6). Indeed, the non-linear dependence of the total HOM on the turnover
251 in Figure 3B requires at least a second oxidation step and explains the dependence of
252 the α-pinene SOA yield on [OH], contributing to the OH scavenging effect.
253 The mechanism of product scavenging via dimer suppression by short chained peroxy
254 radicals or HO_2 is general for peroxy radical chemistry and is not limited to the
255 presence of isoprene in the mixture. It is effective in mixtures of α-pinene with CO
256 via HO_2 (Figure 4) and with CH_4 via CH_3O_2 radicals (Figures S7). CO and CH_4 are
257 extreme cases, each with essentially no SOA yield. In both cases, the scavenging
258 effects are solely related to gas-phase chemistry and independent of aerosol
259 composition: organic or inorganic neutral or inorganic acidic particles. We therefore
260 conclude that product scavenging effect is a general effect in mixtures of VOC.
261
262 **Atmospheric implications**

263 Our new findings in JPAC would hold in atmospheric concentration regimes (suppl.
264 section 7). However, in the atmosphere, the OH concentration is not solely controlled
265 by the isoprene / α-pinene ratio as in the JPAC chamber. Simulations using the EMEP
266 MSC-W model[43,44] (suppl. section 8) show that the scavenging effects by isoprene
267 under realistic atmospheric conditions lowers the OH concentration compared to the
268 hypothetical "no isoprene" case and affects the SOA formation. However, even at
269 small isoprene SOA yields, the gains of isoprene SOA and MT-O_3-SOA offset the
270 reduction from OH scavenging (Figure 5, noIso, OHS). When a parameterisation of
271 the product scavenging constrained to our measurements (Figure 2) is included in the
272 global model simulations, we find that photochemically generated MT-OH-SOA is
273 strongly suppressed, in areas with sufficiently high MT and isoprene emissions
274 (Figure 5, PS). The dramatic effects on MT-OH-SOA show the potential for product
275 scavenging to reduce aerosol loadings substantially in many regions of the world,
276 even more so if one considers that product scavenging similarly could also affect e.g.
277 the MT-O_3-SOA (Figure 5, PSox). It is not possible to be so sure about the magnitude
278 of OH scavenging from all potential reactants, since more measurement constraint is
279 needed to include mechanistic descriptions in such systems.
280 Extending our results from mixtures of isoprene, CH_4, and CO with α-pinene or β-
281 pinene to the reactive atmospheric mixture of vapours, any of the reaction products
282 from any of the components in the mixture may react together, such that from the
283 perspective of any of the others, they have been "scavenged" from the mixture.
284 Similarly, from the perspective of the formation of organic particulate material, some
285 of the condensable oxidation products that are direct precursors may be "scavenged",

286 in all cases reducing the ambient yield. Spatial distribution of short chain organic
287 compounds and specific composition of the reaction mixture will determine the
288 strength of the OH and the product scavenging effects. Whilst long lived compounds,
289 like CH_4, may act ubiquitously in cleaner regions of the earth, compounds with strong
290 anthropogenic sources, like CO, may not exert their full scavenging potential because,
291 when high in concentration, they are always accompanied by high concentrations of
292 other pollutants, like NO_X. While oxidant scavenging will take place under nearly all
293 conditions, product scavenging across SOA precursors is a complex function RO_2-
294 terminating agents, such as peroxy radicals of VOC with moderate or no SOA yield,
295 HO_2, and NO_X. Product scavenging and "non-additivity" of SOA yields will thus vary
296 from region to region, accordingly. Without further experimentally constrained
297 parameterisation of the interactions between all relevant components in realistic
298 atmosphere, it is not possible to predict the magnitude and geographical distribution
299 of suppression of SOA formation. Inclusion of explicit interactions of such
300 complexity in global simulations is practically impossible. It is only possible to say
301 for the considered systems that the SOA yields and net SOA mass must be reduced
302 compared to linear addition of yields, even if the control of oxidant were realistically
303 included.
304
305 **Outlook and recommendations**

306 Our findings demonstrate that SOA precursors with modest yields suppress SOA
307 forming products of higher SOA yield precursors substantially. Our work directly
308 challenges two widespread treatments of SOA formation and suggests an alternative
309 mechanistically-based solution. A first obvious recommendation following this work
310 is that the decoupling of the modulation of oxidant fields from SOA precursor
311 turnover is clearly discouraged. We have further demonstrated that simple linear
312 addition of SOA mass from the individual yields of components in a VOC mixture
313 will likely lead to a substantial overestimation of SOA production. Measuring SOA
314 yields with individual compounds leads to insight into the mechanisms of SOA
315 production but the results do not reflect the conditions of the real environment. Such
316 data should therefore be used with caution when modelling aerosol formation. In the
317 general case, the abundance of HOM, HOM-RO_2 and RO_2 products from potential
318 SOA precursors as well as from volatile compounds not producing SOA mass should
319 be considered when predicting the mixture's yield. Our results highlight a need for
320 more realistic consideration of SOA formation in the atmosphere analogous to the
321 treatment of ozone formation, where interactions between the mechanistic pathways
322 involving peroxy radicals are recognised to be essential[23]. It may be possible to
323 produce lumped classes of precursors according to their likelihood of increasing or
324 decreasing a mixture's yield and this could be a focus of further investigation.
325 It is likely that both background oxidant concentrations and VOC emissions (and
326 hence OH reactivity) will change in the future. Without a reasonable representation of
327 SOA yields in different atmospheric VOC mixtures it will not be possible to achieve
328 predictive capability for the SOA contribution to particulate matter.
329

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483 **Supplementary Information** is available in the online version of the paper
484

485 **Author contributions:**
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493 All co-authors discussed the results and commented the manuscript and the
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515 **Data availability statements**
516 All data used are shown as Figures or Tables in the manuscript or in the supplemental
517 information. Raw data are available from the corresponding author on reasonable
518 request.
519

Figure Captions

Figure 1: Reduced *SOA mass* and *yield* of α-pinene by *product scavenging* and *OH scavenging* by isoprene.
The top panel depicts symbolically the transition of the reaction system. **a**: Neutral seed particles: isoprene (red triangles) lowered [OH] (black diamonds) and the corresponding consumption of α-pinene (blue squares), reducing the organic mass dramatically. The organic mass was normalized to sulfate mass (organics/SO_4^{2-}, green circles). The newly discovered product scavenging (red) in the presence of isoprene is separated from OH scavenging (orange) by re-adjustment of [OH]. Because of product scavenging only 60% of the organic mass is formed despite the same α-pinene consumption. (The acidic case is depicted in Figure S3.) Vertical error bars for Δα-pinene and Δisoprene are s.d. for averaging 14-15 samples, horizontal bars show the averaging intervals. For OH we estimate an overall error of ±33%.
b: The SOA yields in presence of neutral ammonium sulfate (blue) and acidic ammonium bisulfate (red) seed particles were calculated at times <u>B</u>, <u>C</u>, and, <u>D</u> as *organic mass/α-pinene consumption* (acidic seed particles, see suppl. section 3). Not only the SOA mass (indicated by the green spheres in the middle) but also its yield decreased strongly (bar plots). <u>B</u> shows the SOA yield for α-pinene alone, while <u>C</u> shows the summed effect of the new product scavenging and OH scavenging in the α-pinene & isoprene reaction system. For the neutral seeds <u>D</u> demonstrates the magnitude of the product scavenging effect on the SOA yield, as [OH] and α-pinene consumption were re-adjusted to the same levels as before isoprene addition. On acidic seed aerosol (red) isoprene makes a substantial contribution to SOA, which compensates for some of the OH scavenging effect and most of the product scavenging effect. The errors reflect the estimated overall 15% uncertainty for an individual experiment.

Figure 2: The reduction of the SOA yield of α-pinene by isoprene as a function of the isoprene/α-pinene consumption (Δisoprene/Δα-pinene).
The actual SOA yield of α-pinene (y_{act} = Δorganic mass / Δα-pinene) in α-pinene & isoprene mixtures was normalized to the average SOA yield obtained with α-pinene-only (y_{AP}) at same conditions for neutral (blue) and acidic seeds (red). The grey area indicates the ±20% band for the scattering of the α-pinene-only yields around y_{AP} = 0.17 which includes the 15% error in the individual SOA mass yields (vertical bars) and the variability of the experimental conditions for the reaction system with α-pinene-only. Horizontal error bars show the uncertainties of the isoprene/α-pinene ratio (±10%) derived from the measurement errors of the compounds.
The dashed line is the fit to the results for the neutral seeds that was implemented in the global model calculations to parametrize product scavenging:
$y_{act} = y_{AP} \cdot (0.48 + 0.52 \cdot exp[-1.53 \cdot (\Delta isoprene/\Delta \alpha\text{-}pinene)])$

564

565 **Figure 3:** HOM monomer/dimer distribution in the presence and absence of isoprene
566 illustrating the product scavenging effect.

567 **a:** comparison of two mass spectra taken in experiments with (orange) and without
568 isoprene (blue). In the presence of isoprene the dimer/monomer drops to about 1/3,
569 indicating that the formation of these extremely low vapour pressure compounds is
570 efficiently suppressed in the presence of isoprene. **b:** Both the total HOM
571 (monomers+dimers, circles) and HOM dimers (squares, molecular mass > 370 Da)
572 decrease with decreasing α-pinene turnover. Here [OH] was varied in two different
573 ways: i) by decreasing the OH production rate, i.e. by decreasing the photolysis of
574 ozone ($J(O^1D)$, blue) and ii) by adding increasing amounts of isoprene (red). In the
575 presence of isoprene HOM decrease more strongly, mainly because the product
576 scavenging is suppressing the α-pinene HOM dimers. The total HOM from the two
577 different experiments were normalized to 1 for better comparison. **c:** Estimate of the
578 product scavenging effect on α-pinene HOM dimers by isoprene at turnover 5.0×10^7
579 cm^{-3} s^{-1} based on molecular mass weighted signals in the mass spectra (details in
580 Figure S8). Data for α-pinene-only were interpolated from the nearest $J(O^1D)$ data
581 (arrows in **b**). The reduction in total HOM mass is 33%, to which dimers (dark green)
582 contribute 26% and monomers 7% (light green). Error bars show the s.d. of the
583 averages over 31 data points. The suppression of α-pinene HOM dimers of 26%
584 explains most of the 35% product scavenging derived from reduced SOA formation in
585 Figure 1. The balance is a result of the reduced yield of HOM monomers and/or shifts
586 in their volatility spectrum.

587

588

589 **Figure 4:** Suppression of α-pinene SOA in presence of CO illustrating the generality
590 of the product scavenging effect.

591 **a:** comparison of three mass spectra taken in experiments with (orange [CO]=10 ppm,
592 red [CO]=57 ppm) and without CO (blue). In the presence of [CO] > 10 ppm the
593 dimer/monomer drops by more than 1/2, indicating that the formation of the dimers is
594 efficiently suppressed in the presence of CO. Because of the high [CO] overall HOM
595 are suppressed by factor of 4 and 5 respectively. **b:** The product scavenging effect
596 reduces the α-pinene yield in the reaction system α-pinene & CO & OH in the
597 presence of ammonium sulfate seeds. The actual SOA yield, calculated as actual
598 organic mass/actual α-pinene consumption, decreases by more than 50%, when 40
599 ppm CO was added to the reaction system. CO concentrations were calculated from
600 known inlet concentration, the flow rate through the RC and the reaction rate of CO
601 with OH. Light colored data points show steady state averages, whereby horizontal
602 error bars show the averaging interval; s.d. of the averages are of the same size or
603 smaller than the symbols.

604 Note, panels **a** and **b** were not taken from the same experiment: experiments to show
605 HOM in the gas-phase and to show SOA suppression cannot be performed in optimal
606 fashion under the same conditions. To measure the unperturbed HOM-MS, particle
607 formation must be avoided. In contrast, mass formation and its suppression must be
608 determined in presence of seed surface as HOM losses at the walls of the chamber
609 have to be minimized. Therefore, the experiment to measure the HOM-MS was
610 performed without seed aerosol whereas ammonium sulfate particles were added to
611 measure the suppression of mass formation by CO. Otherwise the conditions of the
612 experiments were similar.

613

614
615 **Figure 5**: Atmospheric implications of product scavenging and OH scavenging.
616 Global model calculations showing that OH scavenging (OHS) and product
617 scavenging (PS) in presence of isoprene reduce the photochemically derived MT-OH-
618 SOA mass (red) significantly compared to the reference cases NoIso. For the
619 calculation a 4% iSOA yield for acidic aerosols was applied (sum of the brownish
620 bars). OHS is inherently considered in models as long as biogenic SOA (BSOA)
621 formation is directly linked to the oxidant fields, but the new PS effect reduces the
622 MT-OH-SOA even further. To illustrate the maximum potential PS effect it was also
623 applied to ozone derived MT-O_3-SOA (orange, PSOx). In this case the iSOA gain for
624 1% iSOA yield on neutral aerosols (dark brown) would not be able to compensate for
625 the loss of MT-SOA. We show the global average and results for regions with high
626 and low isoprene emissions and high and low population density. The map shows
627 isoprene emissions, green shaded in [mg m^{-2}] and the areas of the selected regions.
628 All contributions are normalised to MT-OH-SOA of the respective NoIso case, when
629 biogenic isoprene emissions were omitted in the model (suppl. section 8).

a

α-Pinene

α-Pinene + Isoprene

α-Pinene + Isoprene OH re-adjusted

Isoprene adjustments

Product scavenging

OH scavenging

Δ α-pinene [ppb]

Δ isoprene

Organics / SO_4^{2-}

OH conc. [cm^{-3}]

Duration since isoprene addition [h]

B   C   D

b

Neutral seed particles

Acidic seed particles

SOA yields

B
α-Pinene
reference

C
Product & OH
scavenging

D
Product
scavenging

B
α-Pinene
reference

C
Product & OH
scavenging

D
Product
scavenging

a "Monomer range" "Dimer range"

b decreasing [OH]

decreasing JO1D

increasing isoprene

α-Pinene turnover: $k_{OH} \cdot [OH] \cdot [\alpha\text{-pinene}]$ [cm^{-3} s^{-1}]

c

JO1D 4.3   ISO 5.0   JO1D 5.7

[$\cdot 10^7$ cm^{-3} s^{-1}]