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1 **Decrease in sulfate aerosol light backscattering by reactive uptake of** 2 **isoprene epoxydiols**

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11 Sulfate aerosol is responsible for a net cooling of the Earth's atmosphere due to its ability to
12 backscatter light. Through atmospheric multiphase chemistry, it reacts with isoprene epoxydiols
13 leading to the formation of aerosol and organic compounds, including organosulfates and high-
14 molecular weight compounds. In this study, we evaluate how sulfate aerosol light backscattering is
15 modified in the presence of such organic compounds. Our laboratory experiments show that reactive
16 uptake of isoprene epoxydiols on sulfate aerosol is responsible for a decrease in light backscattering
17 compared to pure inorganic sulfate particles of **up to - 12 %** at 355 nm **wavelength** and **- 21 %** at 532
18 nm **wavelength**. Moreover, while such chemistry is known to yield a core-shell structure, the
19 observed reduction in the backscattered light intensity is discussed with Mie core-shell light
20 backscattering numerical simulations. We showed that the observed decrease can only be explained
21 by considering effects from the complex optical refractive index. Since isoprene is the most abundant
22 hydrocarbon emitted into the atmosphere, and isoprene epoxydiols are the most important isoprene
23 secondary organic aerosol precursors, our laboratory findings can aid in quantifying the direct
24 radiative forcing of sulfates in the presence of organic compounds, thus more clearly resolving the
25 impact of such aerosol particles on the Earth's climate.

26 **Introduction**

27 Atmospheric aerosols directly contribute to the Earth's radiative balance through light
28 scattering and absorption.¹ Hence, sulfate aerosols produce a net negative radiative forcing²⁻⁵
29 that is attributed to their ability to backscatter solar radiation.⁶ Conversely, the impact of
30 organic aerosol on the Earth's radiative balance remains elusive as it is associated with large

31 uncertainties.⁶⁻¹⁰ While it was assumed that sulfur is primarily present in its inorganic forms
32 (e.g., SO_4^{2-} , HSO_4^- , HSO_3^-), field and laboratory studies¹¹⁻¹⁵ recently showed that organosulfur
33 compounds, including organosulfates, are important contributors to the total sulfate aerosol
34 mass. For example, Surratt et al.¹⁵ have reported that organosulfates can contribute to a
35 substantial fraction of the organic aerosol mass (i.e., up to 30 %). Among the chemical
36 processes leading to organosulfates, recent studies have highlighted the importance of multiphase
37 chemistry (reactive uptake) of isoprene epoxydiols (IEPOX).¹⁶⁻²² Hence, IEPOX have been shown to be
38 key products formed from the hydroxyl radical (OH)-initiated oxidation of isoprene,²³ which is the
39 most abundant non-methane volatile organic compound emitted into the atmosphere.²⁴ Once
40 produced, gaseous IEPOX can undergo acid-driven multiphase chemistry yielding a wide variety of
41 oxygenated compounds including C_5 alkene triols,²⁵ 2-methyltetrols,^{26,27} hemiacetal dimers,²⁸ *cis*-
42 and *trans*-3-methyltetra hydrofuran-3,4-diols,¹⁷ and organosulfates (e.g., IEPOX-OSs),^{11,29-31}
43 contributing to the formation of secondary organic aerosols (SOA). Moreover, the reactive uptake of
44 IEPOX on sulfate aerosol leads to a substantial inorganic-to-organic sulfate conversion (i.e., up to 90
45 %) and increases as a function of IEPOX-to-inorganic sulfate ratio.¹¹ For example, organosulfates have
46 been estimated to account for 16.5 % of the total organic carbon found in fine particulate matter
47 $\text{PM}_{2.5}$ collected from downtown Atlanta, GA.³² IEPOX-OSs (e.g., 2-methyltetrol sulfate isomers)
48 represented in this study, 12.6% of these organosulfates. As an important result, in the presence of
49 acidic sulfate aerosol, IEPOX modifies the aerosol chemical composition, as revealed in recent
50 studies.^{11,21,22,33} For example, a net modification of the aerosol morphology from a well-mixed sphere
51 to a core-shell structure has been reported,^{11,21,22} which is anticipated to impact the aerosol
52 physicochemical properties.¹¹

53 Light backscattering is a physical process sensitive to the aerosol number concentration, size,
54 shape and chemical composition through the particles complex refractive index.³⁴⁻³⁷ Very recently,
55 Reid et al. interestingly showed that light scattering can be used to detect the aerosol morphology of
56 individual particles.³⁸ By light backscattering, we here intend light scattering in the exact (i.e., strict)
57 backward scattering direction of Pi or 180.0° , hence far from the 90 to 170° scattering angles, often
58 reported in the literature as backward scattering direction. Light scattering may indeed vary when
59 the scattering angle differs from the exact Pi backscattering angle, as we demonstrated.³⁹ Moreover,
60 precise knowledge of the backward scattering direction of Pi is required for accurate radiative
61 transfer calculations⁴⁰. Until recently, measuring exact light backscattering by particles embedded in
62 laboratory ambient air represented an experimental challenge, mainly due to the finite size of the
63 detector and the need for a high angular resolution, to specifically address the backward scattering
64 direction with high accuracy ($180.0 \pm 0.2^\circ$). These difficulties have been recently overcome⁴¹ and it is

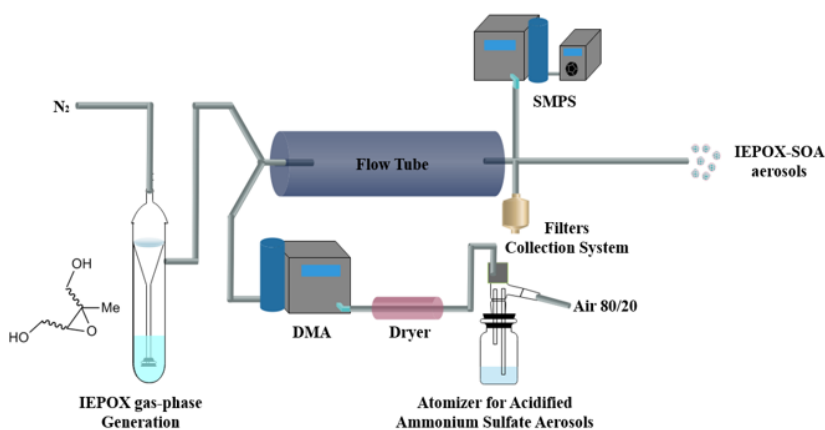
65 now possible to conduct laboratory experiments in order to accurately quantify the light
66 backscattered by aerosols.

67 In this paper, controlled-laboratory experiments were performed to quantify the modification of
68 light backscattering due to the reactive uptake of gaseous IEPOX on acidic sulfate aerosol particles.
69 Hence, acidified ammonium sulfate (AAS) seed aerosols were generated and chemically
70 characterized in the presence and in the absence of IEPOX. To confirm the formation of IEPOX-SOA,
71 the resulting organic products, i.e., organosulfates, were quantified using an ultra-high performance
72 liquid chromatography methodology, interfaced with an electrospray ionization-mass spectrometer
73 (UHPLC/ESI-MS). In the meantime, the ability of IEPOX-SOA to backscatter light was quantified in the
74 exact (i.e., strict) backward scattering direction of P_i , by using a unique optical experimental setup,
75 issued from recent advances in laboratory light scattering by atmospheric aerosols, as stated above.⁴¹
76 We then compare our laboratory findings with the outputs given by Lorenz-Mie light scattering
77 numerical simulations. Our results interestingly reveal that reactive uptake of IEPOX on acidified
78 sulfate particles reduces light backscattering compared to pure inorganic sulfates. This finding
79 suggests that, when organic compounds, including organosulfates and high-molecular weight
80 compounds, are present, the ability of inorganic sulfate particles to backscatter light is greatly
81 decreased.

82 Experimental section

83 Material and instruments

84 Aerosol generation and characterization



85

86 **Figure 1.** Schematic of our laboratory experimental set-up for generating IEPOX- SOA, which is similar to prior
87 studies.^{42,43}

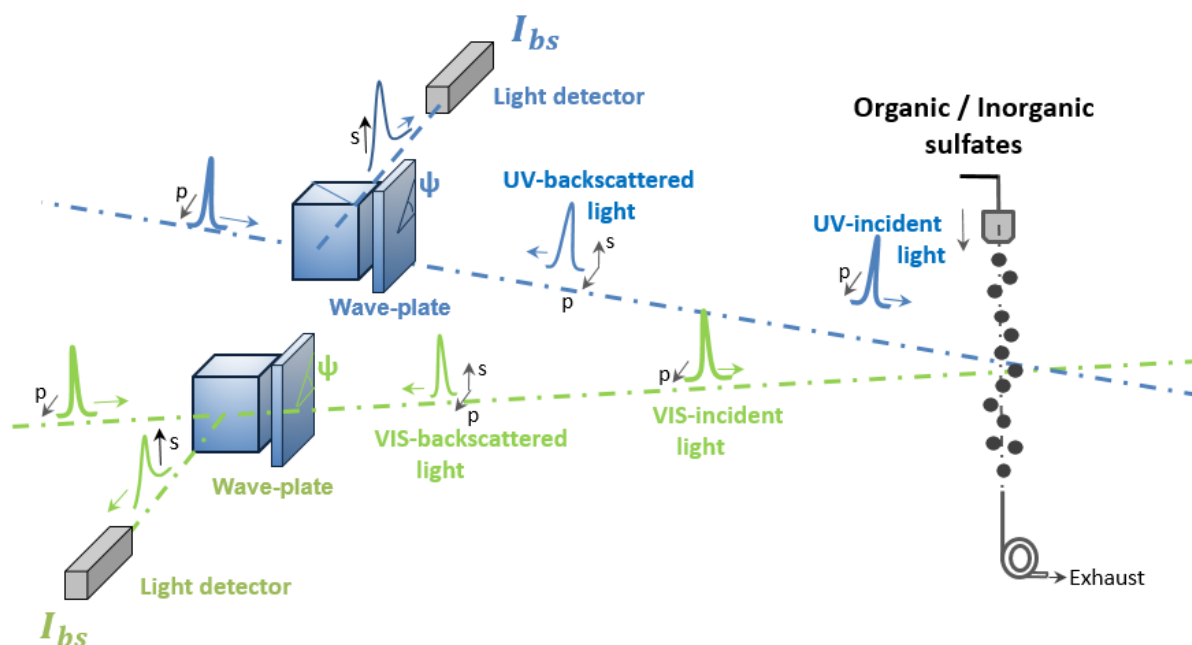
88 Figure 1 presents the flow tube experiment used to generate the IEPOX-SOA and AAS aerosols. The
89 methodology used for the generation of sulfate aerosols and IEPOX were similar to the one
90 previously used,^{42,43} and this chemistry has been shown to produce aerosols with core-shell
91 structures.^{11,21,22} Due to the lack of IEPOX-SOA standards, it was not possible to generate well-mixed
92 aerosols containing IEPOX-derived SOA components. The aerosol seed particles were generated with
93 a constant output atomizer containing AAS. Gas-phase IEPOX was generated after bubbling high-
94 purity nitrogen into a solution of *trans*- β -IEPOX diluted into ethyl acetate; *trans*- β -IEPOX was
95 synthesized in-house as described earlier.⁴⁴ Both were sent through a 6 L large aerosol flow tube
96 reactor. Aerosol particle number, size and volume were determined using a differential mobility
97 analyzer (DMA, TSI Inc, model 3080) coupled with an ultrafine condensation particle counter (CPC,
98 TSI Inc, model 3776). As the particle size modifies the backscattered light intensity, the absence of
99 larger particles (i.e., with diameter > 1 μm) was monitored using an optical particle sizer (OPS, TSI Inc,
100 model 3330). During the IEPOX uptake experiments onto the AAS seed aerosol, the AAS seed
101 aerosols produced from the atomizer were size-selected by a DMA at the entrance of the aerosol
102 flow tube to be centered at 145 +/- 40 nm (Figure S1).

103
104 A synthetic air flow (Air Products, 80/20) of 6 L/min was used, corresponding to a residence time of 1
105 minute in the flow tube reactor. The relative humidity (RH) was held constant at $\sim 49 \pm 3$ % during all
106 the experiments (Figure S2), corresponding to atmospheric daytime conditions in isoprene-rich
107 regions.²¹ The particle number was 10^6 particles per cubic centimeter. The maximum IEPOX gas-
108 phase concentration was 409 ppb and the highest loading for sulfate particles was 2.8×10^4 $\mu\text{g m}^{-3}$.
109 While the concentrations of IEPOX and aerosol seed particles were not atmospherically relevant, the
110 use of these extreme experimental conditions were required to evaluate aerosol light backscattering
111 using the steady-state-of-art instrumentation. After light backscattering, the generated aerosols
112 were collected to quantify the concentration of IEPOX-SOA products by UHPLC/ESI-MS in **negative**
113 **ion mode**. The optically-probed aerosols were sampled at a flow rate of 5.2 L/min onto quartz filters
114 (47 mm diameter - PALL). The detailed methodology used to extract filters has been described
115 previously.⁴⁵ The sample extractions, the operating conditions, the standard preparation, and
116 uncertainty estimates on IEPOX-OSs are described in detail in the supporting information (SI).

117 118 **Light backscattering experiments**

119 Figure 2 shows the schematic of the light backscattering experimental set-up. As extensively
120 described by Miffre et al.,^{39,41} this laboratory experiment consists of a polarimeter operating in the
121 exact backward scattering direction of Pi , defined with a high accuracy ($180.0 \pm 0.2^\circ$), after precise
122 alignment. The backscattered radiation from generated aerosols was discriminated from that due to

123 ambient aerosols as this laboratory experiment is a time-of-flight experiment.^{39,41} As shown in Figure
 124 2 (see prior studies^{39,41} for more details), our laboratory experimental set-up consisted of two
 125 laboratory Pi-polarimeters, one for each wavelength (355 nm, 532 nm), operating simultaneously
 126 with negligible polarization and wavelength cross-talks.⁴¹ Following Figure 2, each Pi-polarimeter was
 127 sensitive to the *s*-polarization component of the backscattered radiation and the corresponding
 128 detected intensity is then hereafter noted I_{bs} where (*b, s*)-subscripts refer to backscattering and to



129 the detected *s*-polarization, respectively. Moreover, for spherical aerosols, which follow the Lorenz-
 130 Mie theory, the polarization state is preserved during the backscattering process. As a consequence,
 131 within our experimental set-up, the whole backscattered intensity can then be detected as I_{bs} when
 132 the incident electromagnetic radiation was *s*-polarized. Besides, when the incident radiation was *p*-
 133 polarized, the detected backscattered intensity I_{bs} canceled if particles were spherical, which
 134 provided a means to follow the particles deviation from isotropy.

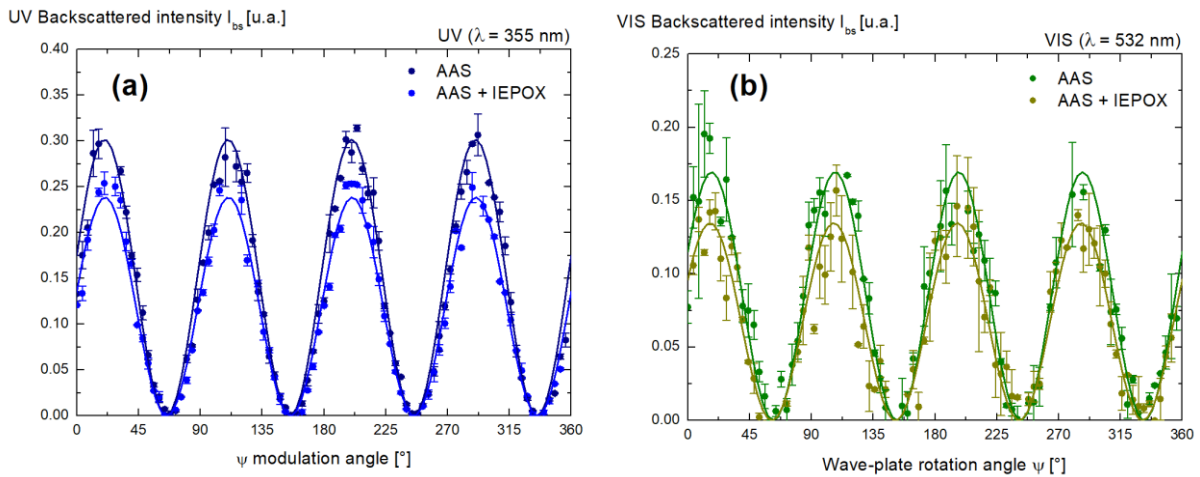
135

136 **Figure 2.** Schematic of our laboratory (UV, VIS) laboratory polarimeter at exact backscattering angle of Pi (180.0
 137 $\pm 0.2^\circ$) for organic / inorganic sulfates embedded in ambient air. As extensively described in Miffre et al.^{39,41,46},
 138 this laboratory experimental set-up, which relies on the robust scattering matrix formalism,⁴⁷ measures the
 139 detected backscattered intensity I_{bs} at two wavelengths (355, 532 nm) for different orientations ψ of a wave-
 140 plate.

141 Results and discussion

142 To gain in accuracy in the evaluation of the backscattered intensity, I_{bs} was recorded for different
 143 incident polarization states, obtained by rotating the ψ -angle of a quarter-wave plate, as displayed in
 144 Figure 3 for inorganic sulfates (AAS particles) at UV and VIS-wavelengths (i.e., 355 and 532 nm,
 145 respectively). Interestingly, the minima of $I_{bs} = f(\psi)$, which corresponded to an incident p -polarized
 146 radiation,⁴¹ were null, thus proving that inorganic sulfate aerosols remained spherical during the
 147 acquisition. As a consequence, the maxima $I_{bs,M}$ of $I_{bs} = f(\psi)$ corresponding to an incident s -
 148 polarized radiation⁴¹ can be used as a metric of the backscattered light intensity by AAS. A precise
 149 evaluation of these maxima was then performed by adjusting our experimental data points with a
 150 $\cos(4\psi)$ curve, as we previously demonstrated for mineral dust,⁴¹ by taking benefit from the robust
 151 scattering matrix formalism.⁴⁷ As a result, within our experimental set-up, the backscattered light
 152 intensity can be precisely evaluated from Figure 3 as $I_{bs,M}$.

153



154

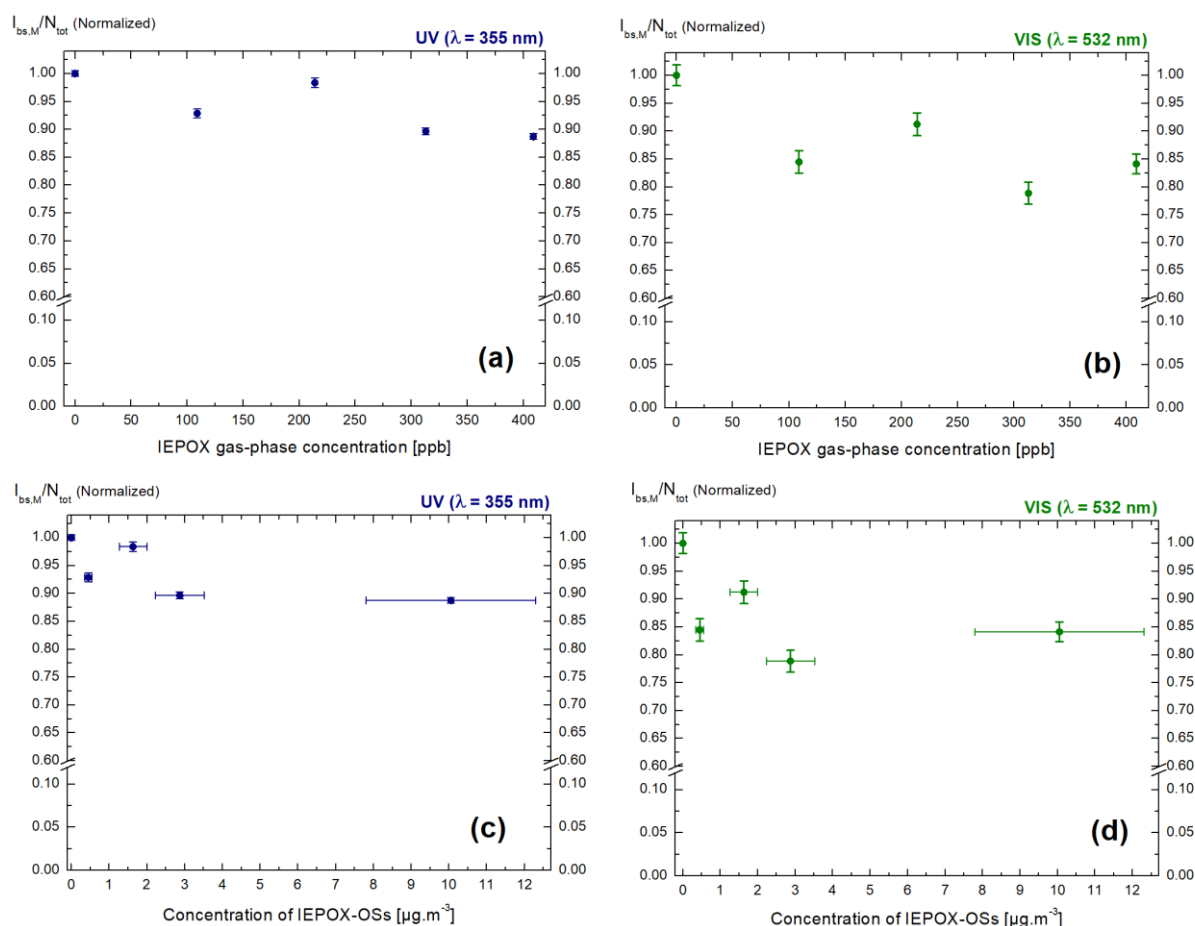
155 **Figure 3: Backscattered intensity acquisition curves: (a)** Detected light intensity I_{bs} backscattered by AAS (0
 156 ppb IEPOX, dark blue), then AAS+IEPOX (409 ppb, blue) at 355 nm wavelength for different orientations ψ of a
 157 wave-plate, error bars are extensively described in a prior work.⁴¹ To reduce statistical error bars, each data
 158 point results from measurement repeated $N (= 5)$ times with corresponding mean and standard deviation. The
 159 variations of $I_{bs} = f(\psi)$ can be adjusted with a $\cos(4\psi)$ curve to precisely evaluate the maxima $I_{bs,M}$ of the
 160 detected backscattered intensity. These maxima, which corresponded to incident s -polarized radiation,
 161 provided precise evaluation of the backscattered intensity. **(b)** Same as (a) at wavelength 532 nm (AAS in dark
 162 green, AAS + IEPOX (409 ppb) in light green).

163

164 The $I_{bs,M}$ maxima were representative of a definite aerosol particle number density, chemical
 165 composition and size distribution. Indeed, if the particles number or the size distribution had varied
 166 during the backscattering experiments, the maxima $I_{bs,M}$ would not have remained constant when
 167 varying the wave-plates orientation. To quantify the modification of the backscattered light intensity

168 I_{bs} through the reactive uptake of IEPOX on sulfate particles, the potential variation in particle
169 number concentrations when considering IEPOX-SOA, instead of inorganic sulfates, was accounted
170 for. For that, $I_{bs,M}$ was normalized by the integral N_{Tot} of the particle number density over the
171 generated particles size distribution, which is described in more detail in the SI. **It should be noted**
172 **that the uptake of IEPOX onto AAS did not change the electrical mobility size distribution of the**
173 **particles; hence the decrease in backscattering is only due to changes in chemical composition.**
174 Measuring the light backscattered by organic-containing aerosol particles is a real experimental
175 challenge due to the very low backscattering cross-section of such laboratory-generated aerosol
176 particles with sizes in the hundreds of nanometers range only. However, the sensitivity achieved in
177 the laboratory backscattering polarimeter was sufficiently high when the experimental conditions
178 were pushed to high-level aerosol concentrations.

179 Figures 4 a,b shows the decrease observed in the normalized backscattered light intensity $I_{bs,M}/N_{Tot}$
180 when increasing the IEPOX gas phase concentration. Within our error bars, it is clear that reactive
181 uptake of IEPOX induces a decrease in the light backscattered by sulfate aerosol. This decrease is
182 found to be slightly more pronounced in the visible spectral range (i.e, -16 % when exposed to gas-
183 phase IEPOX concentrations of 409 ppb at 532 nm wavelength) than in the UV (i.e, -12 % at 355 nm
184 wavelength). Such a spectral dependence may be due to several factors. One possible explanation is
185 that organosulfates or oligomers (high-molecular weight compounds)^{16,17,48,49} absorb UV-light, which
186 may modify the complex refractive index.⁴⁸ However, to be confirmed, this hypothesis would require
187 authentic standards that cannot be synthesized at present, and it is hence beyond the scope of this
188 contribution.



189

190 **Figure 4. (a & b):** Upper Figures: Normalized light backscattered intensity $I_{bs,M}/N_{Tot}$ to account for potential
 191 variability in particle numbers and size distribution as a function of IEPOX gas-phase concentration [ppb] at
 192 wavelength 355 nm (a) then wavelength 532 nm (b). **(c & d):** Lower Figures: Normalized light backscattered
 193 intensity $I_{bs,M}/N_{Tot}$ as a function of IEPOX-OSs mass concentration. The AAS levels remained constant in the
 194 aerosol flow tube reactor. Increasing gas-phase IEPOX concentration corresponds to increasing IEPOX-
 195 OSs/inorganic sulfate ratio. Uncertainties ($\pm 22\%$, see S.M.) are reported for the concentrations of IEPOX-OSs.

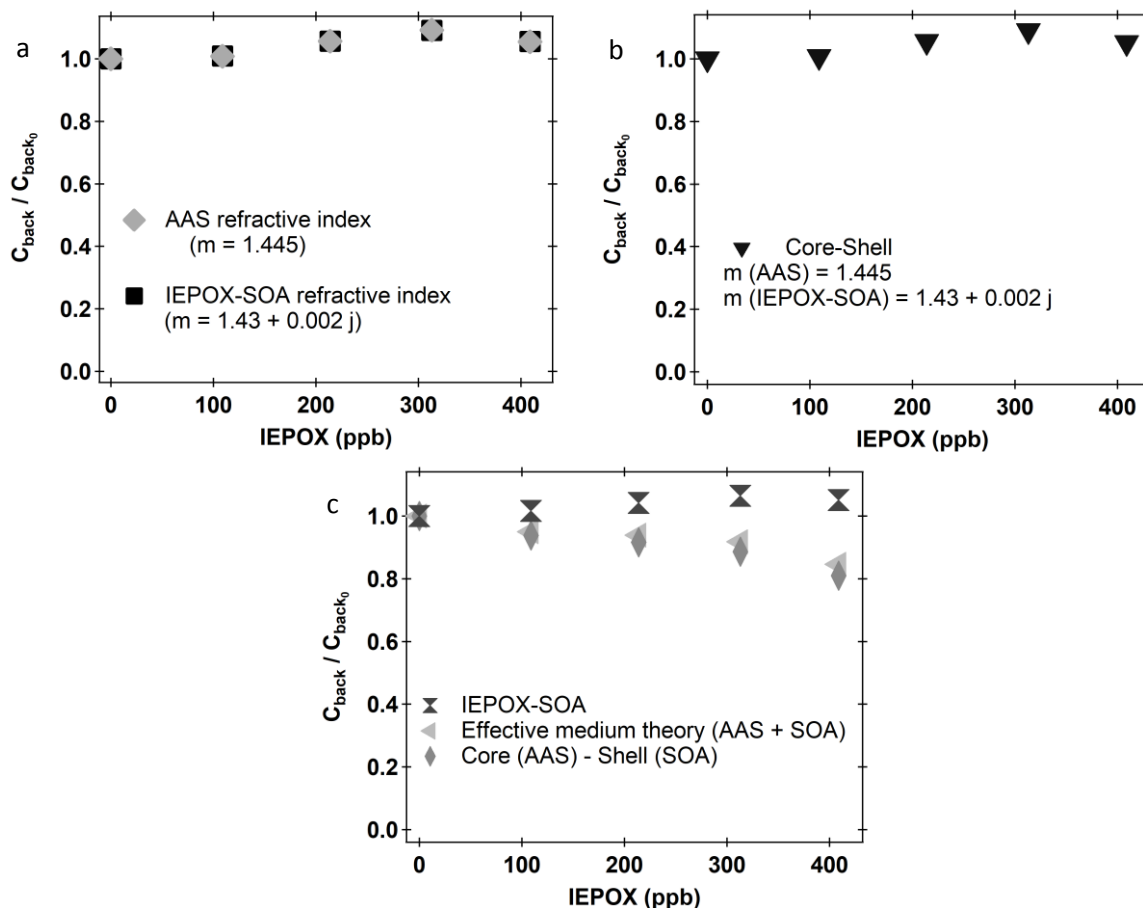
196 Figures 4 c,d present the normalized backscattered intensity $I_{bs,M}/N_{Tot}$ as a function of the IEPOX-
 197 OS mass concentration in the aerosol phase. Within experimental uncertainties, the increase in the
 198 formation of organosulfates is correlated with a decrease in the backscattered light intensity, and
 199 this at both wavelengths. The decrease in the backscattered light intensity is observed even at low
 200 IEPOX-OS concentrations. The IEPOX-OS concentrations generated in the experiments correspond to
 201 a decrease in backscattering light intensity ranging from 2 to 12 % at 355 nm wavelength, and from 9
 202 to 21 % at 532 nm wavelength, as depicted in Figure 4. Though IEPOX-derived OSs represent a small
 203 subset of the total organic mass, the presence of such species, as well as other high-molecular weight
 204 compounds, can reduce aerosol light backscattering.

205 To interpret the observed decrease in light backscattering, light scattering numerical
206 simulations have been performed by applying the Lorenz-Mie theory to compute the backscattering
207 cross-section C_{back} (resp. $C_{back,0}$) of organic (resp. inorganic) particles. Indeed, our laboratory
208 polarimeter showed that the shape of these aerosols remained spherical during the experiments as
209 the minima of $I_{bs,M}$ were null. Then, and as discussed in the introduction, the backscattering process
210 only depends on the aerosol particle number concentration, size distribution (SD) and chemical
211 composition, through the particles complex refractive index. The backscattering cross-sections C_{back}
212 were then computed using the particles SD presented in the SI for the mixture of AAS with IEPOX. As
213 shown in the SI, special care has been taken in our experiments to ensure the SD to be constant
214 during all the acquisitions. As a first step, C_{back} was computed for the refractive index of AAS ($m =$
215 1.445)⁵⁰ and IEPOX-derived SOA ($m = 1.43 + 0.002j$)⁵¹, Figure 5, respectively. Hence, the observed
216 decrease in the backscattering cross-section C_{back} cannot be explained by size effects alone and was
217 therefore related to optical index effects also, as the solutions evolve (Figure 5).

218 To account for the presence of both AAS and IEPOX-derived SOA compounds, we applied
219 effective medium theories, by applying the Aspens formula,⁴⁷ providing the effective particles
220 complex refractive index of a backscattering medium containing a mixture of AAS and IEPOX-derived
221 SOA products. As displayed in Figure 5b however, the variations of $C_{back}/C_{back,0}$ did not more
222 faithfully reproduce our laboratory observations when considering AAS volume fractions in the AAS
223 and IEPOX-derived SOA particle mixtures ranging from 0.96 to 1.00, with 0.02 step, which is
224 consistent with the results from our chemical analyses of the aerosol filter samples. As a result, we
225 investigated the effect on C_{back} of a possible change in the internal structure of the particles. Indeed,
226 the reactive uptake of IEPOX is known to produce core-shell structures.^{11,21,22} To investigate the case
227 of a stratified dielectric sphere (i.e., a spherical inorganic core coated by a spherical organic shell), we
228 applied the numerical code from Toon and Ackermann,⁵² which is an extension of the Lorenz-Mie
229 theory, suitable for thin film absorbent particles as it was expected in our experiments. *When*
230 *adjusting the core/shell radius to consider the above volume fractions, we reproduced a part of the*
231 *observed decrease in C_{back} , as depicted in Figure 5c. Figure 5c shows that considering an IEPOX*
232 *refractive index of $1.43 + 0.5j$ leads to a decrease in the backscattering cross-section $C_{back}/C_{back,0}$*
233 *by about 18 % at 409 ppb at 532 nm wavelength. This trend lies in the same range as the measured*
234 *decrease in light backscattering that reaches 16 % for visible light backscattering (i.e. at 532 nm*
235 *wavelength and 409 ppb of IEPOX). Nevertheless, this decrease in the visible light backscattering can*
236 *also be due to the absorption of high molecular weight compounds as above stated. A plausible*
237 *explanation is that the considered refractive index for IEPOX-derived SOA products reported in the*
238 *literature did not represent our laboratory experimental conditions, where other values for both the*

239 real and imaginary parts of the refractive index were required. To be confirmed, more laboratory and
 240 numerical intensive work on the IEPOX complex refractive index are required to accurately
 241 determine the complex refractive index of IEPOX-derived SOA particles, which is beyond the scope of
 242 this contribution.

243



244 **Figure 5.** Lorenz-Mie light scattering numerical simulation of the backscattering cross-section C_{back} normalized
 245 to $C_{back,0}$ of inorganic particles at 532 nm wavelength, considering the SD given in the S.M. for (a): AAS and
 246 IEPOX-derived SOA refractive index, (b): a core-shell model using the above refractive indices and volume
 247 fractions, (c): a core-shell model, considering $1.43 + 0.5j$ for the IEPOX-derived SOA complex refractive index,
 248 together with $C_{back}/C_{back,0}$ for that refractive index and from effective medium theory.

249

250 Conclusions

251 In this paper, in a context where isoprene epoxydiols are the most important isoprene SOA
 252 precursors, we present an unexpected trend in the backscattering coefficient of SOA containing
 253 sulfate and organics material: in both the UV and VIS spectral ranges, sulfate aerosol light
 254 backscattering is decreased by reactive uptake of IEPOX on acidified inorganic sulfate aerosol

255 particles. This laboratory finding has been obtained by taking advantage of an accurate and
256 extremely sensitive polarimeter operating at the exact backward scattering angle of π as the
257 laboratory-generated particles, whose size lies in the hundreds of nanometer range, exhibited a very
258 low backscattering cross-section. When acidified sulfate particles ($2.8 \times 10^4 \mu\text{g}\cdot\text{m}^{-3}$) were exposed to
259 the largest IEPOX concentration (i.e., 409 ppb), the observed decrease reaches 12 % at 355 nm
260 wavelength and 16 % at 532 nm wavelength. Possible explanations for the observed decrease in light
261 backscattering were investigated using existing literature and Lorenz-Mie light scattering numerical
262 simulations of the particles backscattering cross-section of organic / inorganic particles. We showed
263 that the observed decrease can only be explained by considering effects from the complex optical
264 refractive index. Notably, we discussed that the formation of an inorganic core - organic shell
265 structure can be key for explaining the reported decrease, though effective medium theories may
266 also be key. The formation of a high-absorbing organic coating, corresponding to a large imaginary
267 part of the optical refractive index of IEPOX-SOA of about 0.5, was necessary to explain our
268 experimental results. These results should be improved in laboratory experiments by considering
269 more complex particle chemistry or micro-physical structure. In summary, acid-driven particle-phase
270 and/or heterogeneous chemistry has the potential to change the optical properties of aerosols
271 through both chemical and physical pathways, opening routes for future research. Indeed, the
272 development of such a precise optical system will allow for quantification of the radiative effects of
273 aerosol particles impacted by atmospheric ageing.

274 Author contributions

275 **C. Dubois:** Formal analysis, Visualization, Writing – original draft, **D. Cholleton:** Methodology,
276 Software, Formal analysis, Investigation Visualization, Writing - Review & Editing, **R. Gemayel:** Vi-
277 sualization, **Y. Chen:** Visualization, **J.D. Surratt:** Formal analysis, Investigation, Visualization,
278 Resources, Project administration, Funding acquisition, **C. George:** Methodology, Formal analysis
279 Investigation, Validation, Project administration, Funding acquisition, **P. Rairoux:** Methodology,
280 Formal analysis, Investigation Validation, Project administration, Funding acquisition, **A. Miffre:**
281 Methodology, Formal analysis Investigation, Software, Visualization, Writing – original draft, Writing
282 - Review & Editing Validation, Project administration, Funding acquisition, **M. Riva:** Methodology,
283 Formal analysis, Investigation Visualization, Writing - Review & Editing, Project administration,
284 Funding acquisition.

285 **Conflicts of interest**

286 There are no conflicts to declare.

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294

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