

***INFLUENCES OF UPWIND EMISSION SOURCES AND
ATMOSPHERIC PROCESSING ON AEROSOL
CHEMISTRY AND PROPERTIES AT A RURAL
LOCATION IN THE NORTHEASTERN US***

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39 **Abstract**

40 The occurrence of non-liquid and liquid physical states of submicron atmospheric
41 particulate matter (PM) downwind of an urban region in central Amazonia was investigated.
42 Measurements were conducted during two Intensive Operating Periods (IOP1 and IOP2) that
43 took place during the wet and dry seasons, respectively, of the GoAmazon2014/5 campaign. Air
44 masses representing variable influences of background conditions, urban pollution, and regional
45 and continental scale biomass burning passed over the research site. As the air masses varied,
46 particle rebound fraction, which is an indicator of the mix of physical states in a sampled particle
47 population, was measured in real time at ground level using an impactor apparatus. Micrographs
48 collected by transmission electron microscopy confirmed that liquid particles adhered while non-
49 liquid particles rebounded. Relative humidity (RH) was scanned to collect rebound curves. When
50 the apparatus RH matched ambient RH, 95% of the particles were liquid as a campaign average,
51 although this percentage dropped to as low as 60% during periods of anthropogenic influence.
52 Secondary organic material, produced for the most part by the oxidation of volatile organic
53 compounds emitted from the forest, was the largest source of liquid PM. Analyses of the mass
54 spectra of the atmospheric PM by positive-matrix factorization (PMF) and of concentrations of
55 carbon monoxide, total particle number, and oxides of nitrogen were used to identify time
56 periods affected by anthropogenic influences, including both urban pollution and biomass
57 burning. The occurrence of non-liquid PM correlated with these indicators of anthropogenic
58 influence. A linear model having as output the rebound fraction and as input the PMF factor
59 loadings explained up to 70% of the variance in the observed rebound fractions. Anthropogenic
60 influences appear to favor non-liquid PM by providing molecular species that increase viscosity

61 when internally mixed with background PM, by contributing non-liquid particles in external
62 mixtures of PM, and a by combination of these effects under real-world conditions.

63 **1. Introduction**

64 Particulate matter (PM) directly affects the Earth's climate by scattering and absorbing
65 solar radiation and indirectly by effects on clouds (Ramanathan et al., 2001). The magnitude of
66 these effects depends in part on the physical and chemical properties of the particulate matter
67 (Andreae and Rosenfeld, 2008). The physical state of PM, as liquid or non-liquid, can influence
68 the growth rates of small particles and ultimately the production of cloud condensation nuclei
69 (CCN) (Riipinen et al., 2011; Perraud et al., 2012). Liquid particles pose negligible in-particle
70 diffusion barriers for condensing species and therefore can grow rapidly. By comparison, non-
71 liquid particles, referring to both semisolid and solid particles, can have a different behavior. For
72 some conditions, semisolid particles can grow slowly because of in-particle limits on rates of
73 molecular diffusion, and solid particles can grow even more slowly when limited to surface
74 adsorption (Riipinen et al., 2012; Shiraiwa and Seinfeld, 2012; Li et al., 2015). Liquid compared
75 to non-liquid PM can also affect reactivity (Kuwata and Martin, 2012; Li et al., 2015). The
76 consequences of the differing growth mechanisms can be that the growth of small particles is
77 relatively disfavored in a population of liquid particles of heterogeneous sizes, as compared to a
78 similar population of non-liquid particles (Zaveri et al., 2014). An implication can be that CCN
79 concentrations are ultimately greater for a population of non-liquid particles that grows to CCN
80 sizes, as compared to a population of liquid particles.

81 Secondary organic material (SOM), produced by the oxidation of biogenic volatile
82 organic compounds (BVOCs), is a major source of atmospheric PM, especially over forested
83 regions where SOM often dominates the mass concentration of submicron PM (Hallquist et al.,
84 2009; Jimenez et al., 2009). The physical state of SOM has been studied in both laboratory
85 (Vaden et al., 2011; Kuwata and Martin, 2012; Perraud et al., 2012; Saukko et al., 2012; Renbaum-

86 Wolff et al., 2013; Kidd et al., 2014; Bateman et al., 2015; Li et al., 2015; Liu et al., 2015; Pajunoja
87 et al., 2015; Song et al., 2015) and ambient environments (Virtanen et al., 2010; O'Brien et al.,
88 2014; Bateman et al., 2016; Pajunoja et al., 2016). For background conditions of the Amazonian
89 tropical forest, a region dominated by isoprene-derived SOM and high RH, PM was mostly
90 liquid (Bateman et al., 2016). For a boreal forest in northern Europe, a region dominated by
91 pinene-derived SOM and low RH, PM was largely non-liquid (Virtanen et al., 2010). The
92 combined set of laboratory and ambient studies show that the physical state of PM having high
93 SOM content depends on the surrounding relative humidity (RH). This effect arises in part
94 because organic particles are hygroscopic to various extents depending on composition. Water
95 absorption, which is favored at elevated RH, has a plasticizing effect on physical state (Koop et
96 al., 2011).

97 The physical state of PM affected by urban pollution over forests remains largely
98 unexplored. A single day of ambient observations in central Amazonia suggested that ambient
99 PM affected by urban pollution tended toward a non-liquid state (Bateman et al., 2016), and
100 laboratory studies support the idea of an important modulating role of pollution in the physical
101 state of SOM. A non-liquid state was favored for SOM produced from single-ring aromatic
102 species (Liu et al., 2015; Song et al., 2015) as well as mixed with polycyclic aromatic
103 hydrocarbons (PAHs) (Zelenyuk et al., 2012; Abramson et al., 2013). Organic molecules
104 associated with urban pollution and industrial activities tend to be less hygroscopic than biogenic
105 SOM (Hersey et al., 2013). When internally mixed within biogenic SOM, the anthropogenic
106 molecules have a tendency to reduce water uptake and thereby reduce the viscosity of the mixed
107 particles. A similar line of reasoning leads to an identical hypothesis for the effects of biomass
108 burning emissions. Compared to prevailing background conditions of SOM dominance over

109 many forests, PM produced by biomass burning leads to a net effect of decreased water uptake
110 when the PM mixes into the background particle population (Dusek et al., 2011).

111 The data sets presented herein provide observational evidence on the effects of
112 anthropogenic influences on the physical state of ambient particulate matter. All other factors
113 being equal, the lack of particle rebound is an indicator of liquid PM (Bateman et al., 2015).
114 Conversely, the occurrence of particle rebound is an indicator of non-liquid PM. Rebounding and
115 adhering particles were separately collected for conventional and chemical imaging. The data
116 sets were collected during the two Intensive Operating Periods (IOP1 and IOP2) of the
117 GoAmazon2014/5 experiment, corresponding to the wet and dry seasons, respectively (Martin et
118 al., 2016). The research site (-3.2133°, -60.5987°), called “T3”, was located 70 km downwind of
119 the city of Manaus, population two million, in central Amazonia. Air masses representing
120 background conditions, urban pollution, and regional and continental scale biomass burning
121 passed over the research site. Herein, anthropogenic influence refers to all but background
122 conditions. Under background conditions, the submicron PM in this region is dominated by
123 biogenic SOM (Chen et al., 2009; Chen et al., 2015).

124 **2. Experimental**

125 An impactor apparatus was used for the study of particle rebound (Bateman et al.,
126 2014; Bateman et al., 2015; Bateman et al., 2016). The apparatus was housed inside a
127 temperature-controlled research trailer at the T3 site. Particulate matter was sampled at 5 m
128 above ground through copper tubing having an outer diameter of 13 mm (0.5 inch). In sequence,
129 a drying unit reduced the sampled flow to 25% RH or lower, a Differential Mobility Analyzer
130 (DMA, TSI 3085) selected a subpopulation of dried particles having a narrow distribution of
131 electric mobility, and a humidification unit (Nafion tubes; Perma Pure, MD 110) elevated the RH

132 of the mobility-filtered flow to the targeted RH of a measurement. The drying unit consisted of a
133 Nafion drier in series with a silica gel diffusion drier, and the silica gel was replaced every two
134 days. After passing the dryer, DMA, and humidifier, the resulting flow was split and passed
135 through three impactors operated in parallel. Labels *i*, *ii*, and *iii* refer to each of the three
136 impactors. Each impactor was operated at a flow rate of 1.0 Lpm, corresponding to a setpoint
137 aerodynamic diameter d_a^* of 84.9 ± 5.4 nm (Bateman et al., 2014). Particle number
138 concentrations, denoted by N_i , N_{ii} , or N_{iii} , exiting the impactors were measured by three
139 independent condensation particle counters (CPC, TSI 3010). Measurements were conducted
140 from February 14 to March 16, 2014, during IOP1 and from September 4 to October 15, 2014,
141 during IOP2.

142 The three impactors differed from one another by having uncoated, coated, or no
143 impaction plate. The impactor having the uncoated plate passed both non-impacted and
144 rebounded particles. The impactor having the coated plate (Dow Corning High-Vacuum Grease)
145 passed only non-impacting particles. The impactor having no plate passed all particles. Its
146 purpose was to serve as a compensation arm for possible miscellaneous particle losses, such as
147 wall loss. Based on the particle number concentrations measured downstream of the impactors,
148 the rebound fraction was calculated as follows (Bateman et al., 2014):

149
$$f = \frac{N_i - N_{ii}}{N_{iii} - N_{ii}} \quad (1)$$

150 The terms N_i , N_{ii} , and N_{iii} represent the particle number concentration measured downstream of
151 the impactors having uncoated, coated, and no impaction plate, respectively. The standard
152 deviation of the rebound fraction was based on error propagation for an uncertainty in N of $N^{1/2}$
153 (Agarwal and Sem, 1980).

154 A rebound curve representing $f(\text{RH})$ constituted an individual data set. For most
155 measurements, the DMA setting for electric mobility was held constant (typically 190 nm), the
156 RH in the humidification unit was changed stepwise every few minutes, and f was continuously
157 recorded. Additional protocols of DMA settings and RH profiles were used in a few cases. All
158 protocols, including differences between IOP1 and IOP2, are described in Section S1 of the
159 Supplement.

160 In conjunction with the rebound measurements, particles were collected for imaging by
161 transmission electron microscopy (TEM) and scanning transmission X-ray microscopy (STXM).
162 Images in some cases can directly suggest the liquid or non-liquid state of individual particles
163 (O'Brien et al., 2014; Wang et al., 2016). Samples for imaging were collected as follows. A fourth
164 impactor was added in parallel with the other three impactors. Imaging substrates were affixed to
165 the impaction plate, and multiple substrates were mounted to the plate for concurrent collection
166 for the various microscopy techniques. Substrates included grids coated with Formvar (EMJapan
167 Co., Tokyo, Japan) or lacey carbon (Ted Pella Inc., USA) for TEM and silicon nitride membrane
168 windows (Silson, UK) for STXM. The flow rate and setpoint aerodynamic diameter of the fourth
169 impactor were the same as for the other three impactors. The collected particles represented
170 those that adhered to the substrate at impact, and an assumption in the analysis is that rebound
171 from the substrate was similar to that from the uncoated plate. The flow through this fourth
172 impactor was pulled by an in-line TEM autosampler (Arios Inc., Tokyo, Japan (Adachi et al.,
173 2014)). In this way, the setup separately collected particles that adhered to the grids on the
174 impaction plate and particles that rebounded from the impaction plate and passed to the
175 autosampler. The autosampler collected particles having aerodynamic diameters from 60 to 350
176 nm. Particles adhered to the TEM substrates in the autosampler yet rebounded from the TEM

177 substrates in the impactor because of the significantly different particle impact velocities
178 between the two impactors (i.e., cut-point and impactor design). Samples were collected for
179 TEM analysis between September 30 and October 15, 2014. Samples were collected for STXM
180 analysis between 1:00 and 10:00 (UTC) on October 1, 2014.

181 Microanalysis of individual particles of the collected PM was performed using two
182 instruments: (1) a transmission electron microscope (TEM; JEOL, JEM-1400) equipped with an
183 energy-dispersive X-ray spectrometer (EDS; Oxford Instruments) and (2) a scanning
184 transmission X-ray microscope interfaced for near-edge X-ray absorption fine structure
185 spectroscopy (STXM/NEXAFS; Advanced Light Source, Berkeley). For TEM, imaging was by
186 bright-field microscopy, and particle composition was investigated by EDS. For STXM, at a
187 fixed photon energy an image was obtained by detecting the transmitted light at each pixel while
188 raster scanning the sample. Spatially resolved NEXAFS spectra were obtained from a set of
189 images recorded at different photon energies. The NEXAFS spectra provided chemical bonding
190 information and quantitative elemental ratios (Moffet et al., 2010a;Moffet et al., 2010b;O'Brien
191 et al., 2014;Piens et al., 2016). Section S2 of the Supplement presents further technical
192 information concerning the TEM and STXM/NEXAFS analyses.

193 Additional co-located measurements used in the data analysis herein included a High-
194 Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS; Aerodyne Inc.) (Hu et al., 2015;de
195 Sá, 2016;Hu et al., 2016), a Single-Particle Soot Photometer (SP2; Droplet Measurement
196 Technologies), a size-resolved Cloud Condensation Nuclei Counter (CCNC; Droplet
197 Measurement Technologies, CCNC-100) (Thalman, 2016), a Condensation Particle Counter
198 (TSI, CPC 3772) for measuring particle number concentrations, an Integrated Cavity Output
199 Spectroscopy (ICOS; Los Gatos) for measuring carbon monoxide (CO) concentration, and a

200 Trace Level Enhanced detector (TLE; Thermo Scientific, Model 42i, with further customization)
201 for the measuring concentrations of nitrogen oxides (NO_y). The latter three instruments were
202 deployed at the T3 site as part of the USA Department of Energy (DOE) Atmospheric Radiation
203 Measurement (ARM) Climate Research Facility, including the ARM Mobile Facility One (AMF-
204 1) and the Mobile Aerosol Observing System (MAOS) (Mather and Voyles, 2013; Martin et al.,
205 2016). This facility also collected the meteorological data used herein, including temperature,
206 relative humidity, wind direction, and wind speed. The AMS measured the chemical composition
207 in real-time of non-refractory submicron particles (DeCarlo et al., 2006). The high-resolution
208 data of the organic component in “V-mode” was used in conjunction with positive-matrix
209 factorization (PMF) analysis (Ulbrich et al., 2009) to obtain statistical factors and the associated
210 time series of factor loadings for each season (de Sá, 2016). As a surrogate for concentrations of
211 black carbon, the SP2 measured the time-resolved scattering and incandescence produced by
212 irradiated refractory, light-absorbing components of individual particles having volume-
213 equivalent diameters between 70 and 600 nm (Schwarz et al., 2006; Moteki and Kondo, 2007).
214 The size-resolved CCN activity was obtained by classifying dry particles using a DMA (TSI
215 3081) and then exposing them successively to a range of supersaturations inside the CCNC
216 (Thalman, 2016). The hygroscopicity and CCN activity were analyzed via κ -Köhler theory,
217 which relates particle critical supersaturation to the initial dry diameter and hygroscopicity
218 (Petters and Kreidenweis, 2007; Petters et al., 2009).

219 **3. Results and Discussion**

220 *3.1 Rebound Observations*

221 Particle rebound or particle adhesion at impact depends on the balance of energies.

222 Particle rebound occurs when the kinetic energy before impact is greater than the sum of

223 dissipation and surface adhesion energies after impact (Tsai et al., 1990; Bateman et al., 2014).
224 The dissipation energy of liquid particles is much greater than that of solid particles because of
225 additional mechanisms of dissipation available to the former. Calibration of the impactor shows a
226 transition from rebound to adhesion between 10^2 to 1 Pa s in viscosity for sucrose particles
227 (Bateman et al., 2015).

228 The rebound curves of particles of 190-nm mobility diameter are shown in Figure 1a for
229 IOP1 and IOP2. For $RH < 50\%$, the rebound fraction was between 0.8 and 1.0. For $RH > 50\%$,
230 the rebound fraction decreased monotonically to a low value, typically zero. The shape of the
231 rebound curve in Figure 1a is similar to that for particles of secondary organic material produced
232 in the Harvard Environmental Chamber (Bateman et al., 2015). The rebound fraction of SOM
233 particles produced from isoprene or α -pinene became zero for $RH > 90\%$.

234 The subset of the data for which the apparatus RH matched the ambient RH is shown in
235 Figure 1b (cf. Section S3 of Supplement). In light of the distribution of ambient RH values (cf.
236 Figure 1c), the data set in Figure 1b implies that submicron PM in this tropical environment was
237 liquid most of the time. Bateman et al. (2016) reported such a result for observations under
238 background conditions at this site for data sets collected in 2013 a few months before
239 GoAmazon2014/5 began. The present results reported for GoAmazon2014/5 represent a longer
240 time series (i.e., 550 compared to 30 rebound curves) and reinforce the generality of the earlier
241 result of Bateman et al. (2016) of the prevalence of liquid PM for this forested region under
242 background conditions.

243 In the larger set of observations of the present study, what also emerges is that the
244 rebound fraction remained in median at 0.05 even at 95% RH, implicating the presence of
245 externally mixed PM in the atmosphere. Approximately 5% of the particles were non-liquid even

246 to 95% RH in both the wet and dry seasons (i.e., IOP1 and IOP2) (Figures 1a and 1b). At times,
247 rebound fractions of up to 0.4 occurred for RH > 90%. Elevated rebound fractions were observed
248 more frequently in IOP2 than IOP1. During IOP2, which was extensively influenced by biomass
249 burning, non-liquid particles in median constituted a fraction of 0.3 at 70% RH and a fraction of
250 0.1 at 90%. These RH values prevailed approximately 10% of the time. Events of elevated
251 rebound fraction were associated with the pollution plume from Manaus during IOP1 in the wet
252 season and with both this urban plume as well as increased regional biomass burning during
253 IOP2 in the dry season (cf. Section 3.2).

254 Probability density functions (PDF) of rebound fraction at 75% RH based on the data
255 sets of Figure 1a are shown in Figure 2 for (a) IOP1 and (b) IOP2 for three types of air masses
256 during day and night time periods. Daytime represents 12:00 to 16:00 (local time) (16:00 to
257 20:00 UTC) and nighttime represents 23:00 to 04:00 (local time) (03:00 to 08:00 UTC). Air
258 masses were identified as background, as influenced by local to regional biomass burning, or as
259 influenced by Manaus pollution. The classification scheme was based on concentration regimes
260 of particle number, carbon monoxide, and odd nitrogen (NO_y), as presented in Section S4 of the
261 Supplement. Background conditions included contributions both from natural processes and
262 from the long-distance transport and extensive oxidation of biomass burning emissions (Chen et
263 al., 2009; Martin et al., 2010). Natural processes in this region were dominated by the production
264 of secondary organic material from oxidation of plant emissions (Martin et al., 2010; Poschl et
265 al., 2010). Figure 2a shows that the mode value of the PDF shifted higher under the influence of
266 Manaus pollution compared to background conditions, meaning that rebound became more
267 probable and indicating an increasing presence of non-liquid PM at 75% RH. In Figure 2b, the
268 mode value shifted even higher under the influence of biomass burning. For each type of air

269 mass, the nighttime mode values were higher than the daytime equivalents. The day-night
270 differences were lowest under background conditions.

271 The increase in rebound at night might be explained by a combination of interacting
272 factors. A shallow stable nocturnal boundary layer can trap and thereby concentrate
273 anthropogenic non-liquid particles emitted at night from local emissions, including smoldering
274 fires during IOP2. During the day, the boundary layer expands and dilution is more effective. In
275 addition, the production of liquid secondary organic material by biogenic processes is
276 comparatively more rapid.

277 For further analysis, the rebound curves recorded under background conditions were
278 averaged separately for IOP1 and IOP2 (cf. Figure 1a and Section S5 of the Supplement). These
279 two background-average curves served as references against which deviations in rebound
280 fraction were calculated for all air masses. Rebound deviation represents the excess non-liquid
281 PM over background conditions after detrending the data for the dependence on relative
282 humidity. The rebound deviations for IOP1 and IOP2 are plotted in Figure 3. Rebound deviations
283 as high as +0.5 in rebound fraction were observed. Statistics of Figure 3 are summarized in Table
284 S1, including for the subset of measurements matched with the ambient RH. For the full set of
285 data, including the full range of RH, rebound deviations greater than 0.1 represented 17% and
286 35% of the observations during IOP1 and IOP2, respectively. These deviations, corresponding to
287 increased rebound and thus indicating an increasing presence of non-liquid PM, corresponded to
288 the anthropogenic influences, as developed further in Section 3.2.

289 3.2 *Relationships between Rebound and Other Observations*

290 3.2.1 Case Studies

291 Transitions between background and polluted conditions across 24 hour-periods are
292 presented in Figure 4 as representative examples for each IOP. The bottom panel shows the
293 deviation in rebound fraction relative to the background-average curve (cf. Section S5 of
294 Supplement). Color coding distinguishes relative humidity. From bottom to top, other panels in
295 the figure show temperature, wind direction, wind speed, relative fractions of two groups of
296 AMS PMF factor loadings, black carbon (BC) concentration, sulfate concentration, and total
297 submicron PM mass concentration. Processes contributing to the loading of PMF group A are
298 largely associated with the background atmosphere of Amazonia, including the possibility of
299 long-range transport and extensive oxidation of biomass burning emissions. Processes
300 contributing to the loading of PMF group B are largely associated with urban pollution and local
301 and regional biomass burning (cf. Section S6 of Supplement).

302 Shifts in the deviation in the rebound fraction from the background-average curve are
303 apparent in the time series in the bottom panels of Figure 4. At these times, the fractional loading
304 of PMF group A decreased and that of PMF group B increased, indicating a shift away from
305 background conditions. Background conditions were characterized by high loadings of PMF
306 group A and small rebound deviations. In the left panel (IOP1), in an example of one type of an
307 anthropogenic event, black carbon concentration and the fractional loading of PMF group B
308 abruptly increased together. The rebound deviation simultaneously increased, indicating an
309 increasing presence of non-liquid PM, especially above 70% RH. In the right panel (IOP2), in an
310 example of a second type of an anthropogenic event, the background air mass was gently
311 replaced by an air mass characterized by small increases in rebound deviation and fractional

312 loading of PMF group B yet lacking an associated increase in black carbon concentration. In an
313 example of a third type of anthropogenic event, this air mass was later replaced by an air mass
314 characterized by a strong increase in the fractional loading of PMF group B, total PM mass
315 concentration, and rebound deviation. Around 15:00 (UTC), a convective event associated with
316 rainfall decreased temperature, changed wind direction, and increased wind velocity, and
317 background conditions returned.

318 TEM images collected during the time periods of elevated rebound corroborate the
319 foregoing interpretation of liquid and non-liquid PM for adhering compared to rebounding
320 particles. Images of particles that adhered to the TEM substrates in the impactor at 95% RH are
321 shown in Figure 5a. The images were taken at a tilt angle of 60° so that the aspect ratio of the
322 particles could be viewed. The images show that most adhering particles spread out across the
323 substrate, indicating flattening upon impact, as expected for liquid particles. Some of these
324 adhering particles had a mixed composition, appearing as solid cores surrounded by halos of
325 flattened liquid shells. The horizontal dimensions of the flattened particles approached 1 to 2 μm
326 for vertical dimensions of tens of nanometers. Pöschl et al. (2010) previously recorded similar
327 images for ambient particles in the wet season of 2008 in central Amazonia during the
328 Amazonian Characterization Experiment (AMAZE-08) (Martin et al., 2010). For comparison to
329 the images of the adhering particles, images of particles that rebounded at 95% RH from the
330 impaction plate are shown in Figure 5b. These particles were collected downstream of the
331 impactor. The images show that these particles had high vertical dimensions and spherical or
332 dome-like morphologies and thus suggest that the particles experienced little deformation upon
333 impact, as expected for solid particles.

334 3.2.2 Descriptive Statistics

335 The results of Figures 3 and 4 are further analyzed in Figure 6. Statistics of rebound
336 deviation are shown by box-whisker representation for different windows of relative humidity.
337 The data sets were segregated for presentation by IOP1/IOP2, daytime/nighttime, and air mass
338 type. For background conditions, the rebound deviations relative to their average were mostly
339 zero, indicating that there was low variability among different background air masses. The
340 exception was for the night periods of IOP1. By comparison, under anthropogenic influences, the
341 rebound deviation was positive for both IOPs. Positive deviations were most significant between
342 65% and 95% RH. In all cases, the nighttime deviations were greater than the daytime
343 counterparts. For IOP2, the prevalence of biomass burning confounded separate classifications of
344 urban pollution and biomass burning, and a classification of biomass burning took precedent.
345 Rebound deviations were strongest during these time periods. Statistics of the analysis are further
346 summarized in Table S2 (cf. Section S7 of Supplement).

347 3.2.3 Statistical correlations

348 Scatter plots of rebound deviation with environmental variables of ambient temperature,
349 wind speed, and wind direction show no correlation for both daytime and nighttime datasets (cf.
350 Figure S1 of the Supplement). Scatter plots of rebound deviation with some possible
351 anthropogenic influences are presented in Figure S2. Soot, typically characterized by a solid core
352 region of black carbon, is expected in abundance both in urban pollution and biomass burning
353 emissions. There was, however, no correlation between rebound deviation and black carbon
354 concentrations. There was also no correlation between rebound deviation and total particle mass
355 concentration. Rebound deviation and sulfate concentration weakly anti-correlated, which might
356 be expected given the hygroscopicity of sulfate. Sulfate concentrations, however, were a poor

357 indicator of anthropogenic influence in this region because the variability in background
358 concentrations was comparable in magnitude to any urban influence (de Sá, 2016). As a caveat,
359 an assumption in correlation tests is that variance arises from a single variable, and the
360 possibility of two or more contributing or interacting factors is not directly considered.

361 Given that water uptake is an important process for softening organic material, scatter
362 plots of the rebound deviation at 75% RH with the hygroscopicity parameter κ are shown in
363 Figures 7a and 7b for the data sets from IOP1 and IOP2, respectively. Lower values of κ
364 represent decreased equilibrium water uptake for a fixed RH (Petters and Kreidenweis, 2007).
365 The plots show that the rebound deviation increased as the κ value decreased, meaning that
366 particles of lower hygroscopicity were less prone to being in liquid form. The apparent shift to
367 higher κ values from IOP1 to IOP2 arose from instrumental methods. During IOP1, κ values
368 were measured using the impactor apparatus at sub-saturated RH (i.e., < 100%) (cf. Supplement
369 S8). During IOP2, κ values were measured using a size-resolved CCN instrument at super-
370 saturated RH (i.e., > 100%) (Thalman, 2016). In principle, the two kinds of κ values should have
371 similar numerical values for water-soluble species (Petters and Kreidenweis, 2007). The
372 observed shift is consistent with a more frequent occurrence of non-liquid particles during IOP2
373 (Pajunoja et al., 2015), in this case as a result of more extensive biomass burning, as well as the
374 possibility of liquid-liquid phase separation (Renbaum-Wolff et al., 2016).

375 3.2.4 Chemical characteristics of rebounded particles

376 An analysis of the relationship between rebound deviation and chemical characteristics is
377 presented in Figure 8 based on the fractional loading of PMF group B. The data sets are
378 segregated for presentation by IOP1/IOP2, daytime/nighttime, and four bands of fractional
379 loading. Within each panel, box-whisker statistics of rebound deviation are shown for different

380 windows of relative humidity, ranging from 50% to 95%. The figure shows that the rebound
381 deviation increased at all RH values as the fractional loading of group B increased. The
382 background-average curve used as the reference for rebound deviation corresponded to a
383 fractional loading of 0.00 to 0.15 for group B or correspondingly of 0.85 to 1.00 for group A. An
384 increasing fractional loading of group B represented greater anthropogenic influence. The
385 inference is that anthropogenic influences, represented by a combination of urban pollution and
386 biomass burning, affected chemical composition in ways that increased the presence of non-
387 liquid PM above 50% RH.

388 Scatter plots between rebound deviation at 75% RH and the fractional loading of group B
389 are shown in Figures 9a and 9b for the data sets of the two IOPs. The data points are colored
390 according to the value of the hygroscopicity parameter κ . The plots show that rebound deviation
391 increased for low hygroscopicity and high fractional loading of group B, in agreement with the
392 presentation in Figures 7a and 7b and Figure 8. Figures 9a and 9b further show in explicit
393 fashion that the highest rebound deviations occurred during time periods affected by biomass
394 burning and urban pollution, as characterized by the lowest values of κ and the highest fractional
395 loadings of group B. Smaller κ values for lower fractional loadings of group B can be explained
396 by the differences in O:C ratios between group A and B (Massoli et al., 2010): the O:C ratios
397 were 0.95/0.95 (IOP1/IOP2) and 0.42/0.54 for groups A and B, respectively.

398 A model to predict rebound deviation based on chemical characteristics was constructed.
399 The fractional loadings of PMF group A and B were used as model inputs, and model
400 coefficients represented the effects of RH across nine bands (cf. Section S9 of the Supplement).
401 The observed and predicted rebound deviations are plotted in Figure 10. The corresponding
402 coefficients R^2 of determination were 0.65 and 0.72 for IOP1 and IOP2, respectively. Predicted

403 values were biased high for low rebound deviation and biased low for high rebound deviation.
404 The magnitudes of the model coefficients represented the relative importance of the two PMF
405 groups in predicting rebound deviation (Table S4). In this regard group B dominated during both
406 IOPs. This result is consistent with the role of anthropogenic influences in shifting the PM
407 population to fewer liquid particles and more non-liquid particles.

408 Analysis by STXM/NEXAFS supports the foregoing narrative of anthropogenic
409 influence as a modulator between liquid and non-liquid PM. Rebounded particles were collected
410 on October 1 during a time period classified as influenced by biomass burning emissions. The
411 carbon K-edge spectrum is shown in Figure 11a, and the STXM image is shown in Figure 11b. A
412 notable feature of the NEXAFS spectrum of the rebounded particles is the strong double bond.
413 Pöhlker et al. (2012) previously collected NEXAFS spectra for samples collected at a
414 background site in central Amazonia, and the strong feature of a double bond was absent. The
415 spectra instead resembled those of different types of reference biogenic secondary organic
416 material.

417 For comparison to the spectrum collected of the rebounded particles, carbon K-edge
418 spectra are shown for carbonaceous particles collected in other field and laboratory studies.
419 Based on these results as well as those of the rebound measurements, a hypothesis of soot or
420 black carbon to explain the rebounding particles was ruled out on three grounds. The double-
421 bond feature was homogeneously distributed throughout the particles (Figure 11b) compared to
422 inclusions that are typical for soot (Moffet et al., 2013;Knopf et al., 2014;O'Brien et al., 2014),
423 rebound deviation and black carbon concentrations did not correlate (Figure S2), and the
424 spectroscopic signatures of rebounded particles and soot did not match (Figure 11a). A
425 hypothesis of VOC-derived secondary organic material, including possible changes because of

426 shifts from HO₂ to NO-dominant chemistry (Liu et al., 2016a;Liu et al., 2016b), was also
427 eliminated by comparison of the NEXAFS spectrum of the rebounded particles to the reference
428 spectra for laboratory samples. An important caveat to these interpretations is that some of the
429 hypotheses ruled out for this particular day might still have a role to play on other days.

430 There was exceptional uniformity in the particle population characterized by
431 STXM/NEXAFS, which could suggest that the rebounding PM represented distant sources or
432 alternatively a strong single nearby source. The gray region around the red line in Figure 11a
433 illustrates the low variability across the population of analyzed particles (Figure 11b). Moreover,
434 the variability in the O:C ratio determined by the NEXAFS analysis was just ± 0.01 for O:C =
435 $0.34 (\pm 0.03) [\pm 0.01]$, where the value in parentheses was the uncertainty of the measurement
436 and the value in the bracket was the variability across the image in Figure 11b. During the same
437 time period, the O:C ratio of the ambient PM was 0.77 ± 0.04 by AMS measurements. Hence,
438 the rebounding particles were significantly less oxidized, as is consistent with lower
439 hygroscopicity, increased double bond (C=C) content, and increased fractional loading of PMF
440 group B.

441 Several speculations can be made for the origins of the particles leading to the data set of
442 October 1. The chemical constituents giving rise to the double bonds might derive from
443 biological degradation products from incomplete combustion, such as in biomass burning
444 (Tivanski et al., 2007;Keiluweit et al., 2010). Unexplained by this speculation, however, is the
445 absence of a potassium signature in the NEXAFS spectra, which is typical of most biomass
446 burning. Future collection of NEXAFS spectra would be well motivated for the several different
447 types of biomass burning in an Amazonian context, such as from nearby fields, regionally around
448 Manaus, two or three days away from other regions of South America, and up to a week away

449 from Africa. An alternative speculation for this data set is that solid organic particles produced
450 by the impact of raindrops on wet soil surfaces could be making a contribution to the rebounded
451 PM analyzed here (Joung and Buie, 2015). Wang et al. (2016) recently reported detection of the
452 airborne soil organic particles generated by this mechanism over agricultural fields in the central
453 plains of the USA, and the corridor from Manaus to T3 has many agricultural fields. The
454 rebounded particles collected at T3 and the agricultural particles reported in Wang et al. (2016)
455 both had a homogeneous distribution of double bonds and similar elemental ratios and
456 absorption features. Even so, preliminary analysis across the extended data set at T3 between
457 rebound and nearby precipitation did not show a clear correlation. Another speculation relates to
458 the importance of aromatic compounds as hardening agents. Several gas-phase aromatic
459 compounds, laden with double bonds, were measured during IOP1 and IOP2, including toluene,
460 benzene, trimethylbenzene, and xylenes by proton-transfer mass spectrometry (Liu et al., 2016b).
461 Rebound deviation correlated positively with the concentrations of these compounds during both
462 IOPs, and the correlation was stronger during the night. Laboratory studies show that the uptake
463 of polycyclic aromatic hydrocarbons during the formation of biogenic PM can increase the
464 viscosity of the PM (Vaden et al., 2011; Zelenyuk et al., 2012; Abramson et al., 2013; Liu et al.,
465 2015).

466 **4. Conclusions**

467 Under background conditions, particles composed primarily of highly-oxidized biogenic
468 PM were hygroscopic, and they were liquid for the RH values prevailing over Amazonia at
469 surface level. Anthropogenic influences of urban pollution and biomass burning decreased
470 hygroscopicity, and non-liquid PM became more favored. The shift in physical state correlated
471 with decreasing values of the hygroscopicity parameter κ , decreasing O:C elemental ratios,

472 increasing concentrations of C=C functionalities, and increasing fractional loadings of AMS
473 PMF group B, all of which were indicative of anthropogenic influences. These results
474 demonstrate the importance of anthropogenic influences for altering the physical properties of
475 ambient particulate matter over tropical forests.

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Figure Captions

- Figure 1.** Rebound fraction as a function of apparatus relative humidity during IOP1 (blue) and IOP2 (red), corresponding respectively to the wet and dry seasons in central Amazonia. Panel (a) shows all measurements. Panel (b) shows the subset of data for which the apparatus RH matched the ambient relative humidity (cf. Supplement S3). Panel (c) represents the probability density function of relative humidity at the T3 site during the wet and dry seasons of 2014. Points represent rebound measurements for particles having mobility diameters of 190 nm. Statistics of measurements group by relative humidity are represented in box-whisker format. The horizontal line within a box indicates the median of the points, the horizontal lines at the box boundaries indicate quartiles, and horizontal lines most distant from the box indicate 10% and 90% quantiles. For comparison, the black line shows the rebound curve for particles of secondary organic material produced by photooxidation of an isoprene/ α -pinene mixture in the Harvard Environmental Chamber (Bateman et al., 2015).
- Figure 2.** Probability density function of rebound fraction during (a) IOP1 and (b) IOP2 for categorization by type of air mass and time of day: background conditions (green), Manaus pollution (red), and biomass burning (orange). Solid and dashed lines respectively represent daytime (12:00 to 16:00, local time; 16:00 to 20:00, UTC) and nighttime measurements (23:00 to 04:00, local time; 03:00 to 08:00 UTC). Results are shown for an apparatus RH of 75% and for particles having a mobility diameter of 190 nm.

- Figure 3.** Deviation in rebound fraction relative to the average curve for background conditions during (a) IOP1 and (b) IOP2. Red, purple, and green coloring correspond respectively to the RH regions of rebound, transition, and adhesion for the background-average curve. Results are shown for particles having a mobility diameter of 190 nm.
- Figure 4.** Time series of representative species during two pollution events for IOP1 and IOP2 (left and right sides of figures, respectively). “Total mass concentration” plotted in the figure represents the sum of the AMS and black carbon mass concentrations measured for submicron PM. The PMF mass fractions are expressed in relative terms to one another and necessarily sum to unity. Time on the abscissa is expressed in UTC.
- Figure 5.** Representative TEM images of (a) adhering and (b) rebounding PM at 95% RH collected between 14:15 and 18:15 (UTC) on September 30, 2014, during IOP2. The rebound fraction during the time period of collection approached 0.3. The arrows in panel (b) highlight the locations of particles having high vertical dimensions and spherical or dome-like morphologies, as expected for solid particles.
- Figure 6.** Deviation in rebound fraction for categorization by type of air mass and time of day. The box-whisker representation of the 10%, 25%, 50%, 75%, and 90% quantiles of statistics for each RH bin is explained in the caption to Figure 1. Air mass categorization is as for Figure 2. Results are shown for particles having a mobility diameter of 190 nm.

- Figure 7.** Scatter plot of rebound deviation with the hygroscopicity parameter κ for (a) IOP1 and (b) IOP2. For clarity of presentation, data points are shown for apparatus RH values between 73 and 78%, although the trend applies more broadly. As a guide to the eye, in each panel data are divided into four groups, and medians and quartiles of the groups are plotted as black circles and whiskers, respectively.
- Figure 8.** Deviation in rebound fraction for categorization by chemical characteristics. The box-whisker representation of the 10%, 25%, 50%, 75%, and 90% quantiles of rebound fraction is explained in the caption to Figure 1. The chemical characteristics are categorized by the fractional loading of PMF group B as < 0.15 (green), 0.15 to 0.3 (blue), 0.3 to 0.6 (orange), and > 0.6 (red).
- Figure 9.** Scatter plot of rebound deviation with the fractional loading of PMF group B for (a) IOP1 and (b) IOP2. The data points are colored according to the corresponding hygroscopicity parameter κ . For clarity of presentation, data points are shown for apparatus RH values between 73 and 78%, although the trend applies more broadly. As a guide to the eye, in each panel data are divided into four groups, and medians and quartiles of the groups are plotted as black circles and whiskers, respectively.
- Figure 10.** Scatter plot of observed compared to predicted rebound deviation for (a) IOP1 and (b) IOP2. Predictions are based on linear combinations of the loadings of the two PMF groups. The linear coefficients used in the prediction were optimized as a function of RH (Table S4). The solid line represents a one-to-one correlation, and the dashed line represents the best linear fit. Coefficients R^2 of determination were 0.65 and 0.72 for the IOP1 and IOP2 datasets, respectively. Points are color-coded by relative humidity.

Figure 11. STXM/NEXAFS analysis of particles collected after rebound from the impaction plate. Samples were collected between 1:00 and 10:00 (UTC) of October 1, 2014. (a) Carbon K-edge spectrum of rebounded particles (red). Lines at 285.4 and 288.5 eV highlight absorption by double bonds (C=C) and carboxylic acids (-COOH), respectively. The line in the region of 286.5 to 286.7 eV can have contributions from ketones, carbonyl-substituted aromatics, and phenolic species. For comparison, spectra are shown for carbonaceous particles collected in other field and laboratory studies: soil organic particles from central USA (Wang et al., 2016), soot from the ambient environment, atmospheric particles collected at a background site in central Amazonia (Pohlker et al., 2012), and three laboratory samples of secondary organic material. Data sources: isoprene-derived SOM produced under HO₂-dominant conditions (O'Brien et al., 2014); isoprene-derived SOM produced under NO-dominant conditions (O'Brien et al., 2014), and toluene-derived SOM produced under NO-dominant conditions (this study). (b) STXM image from which the NEXAFS spectrum of panel (a) was obtained. Coloring is by red for absorption at 285.4 eV (i.e., double bonds). Coloring is by green for other types of functionalities. The pixelation visible in the image corresponds to the STXM spatial resolution during data collection.

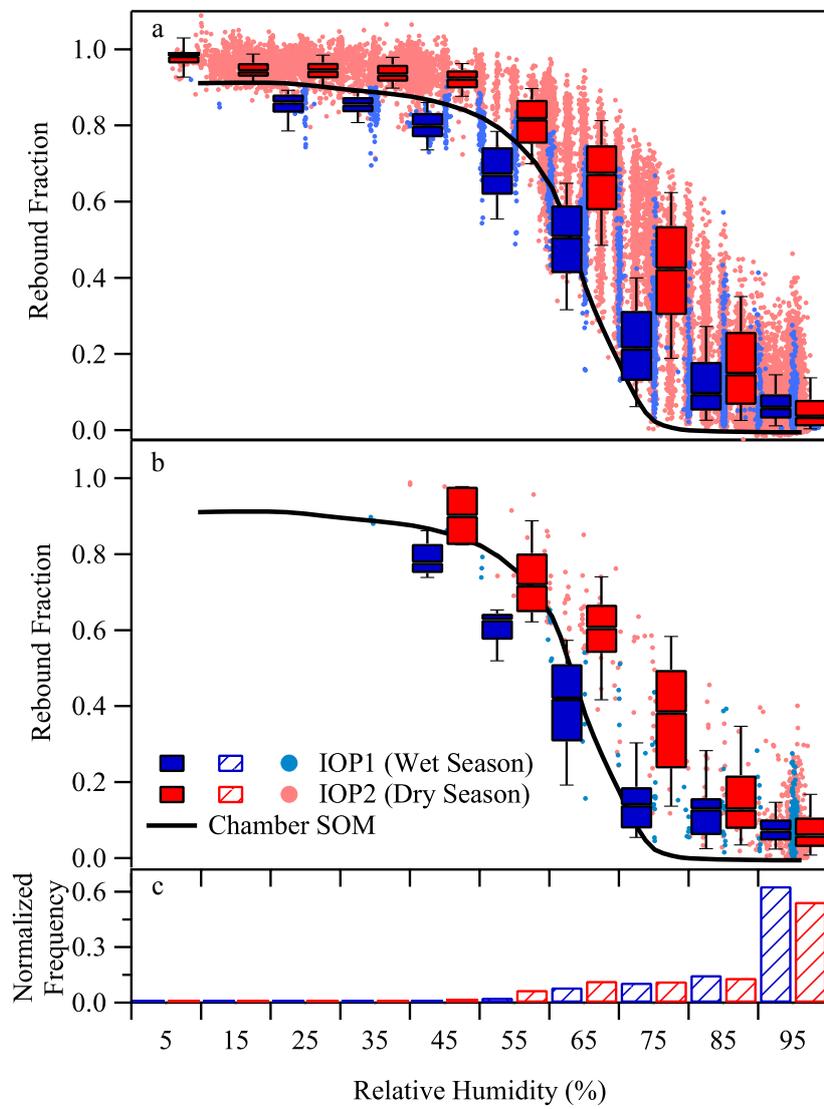


Figure 1

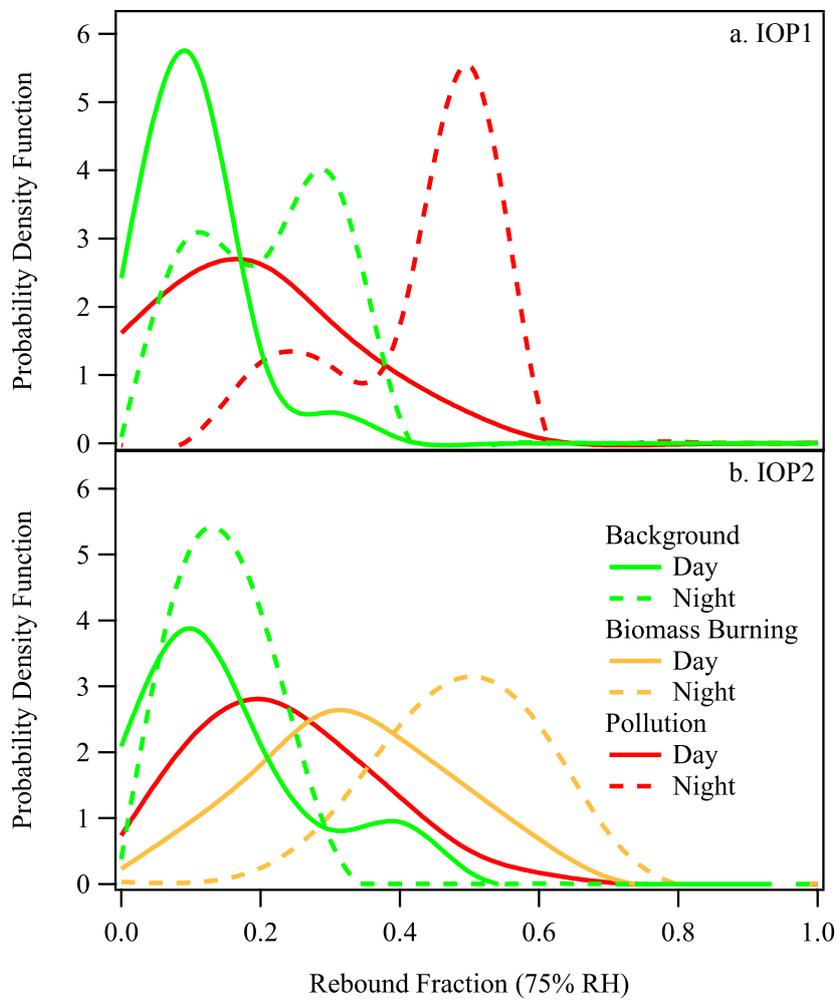


Figure 2

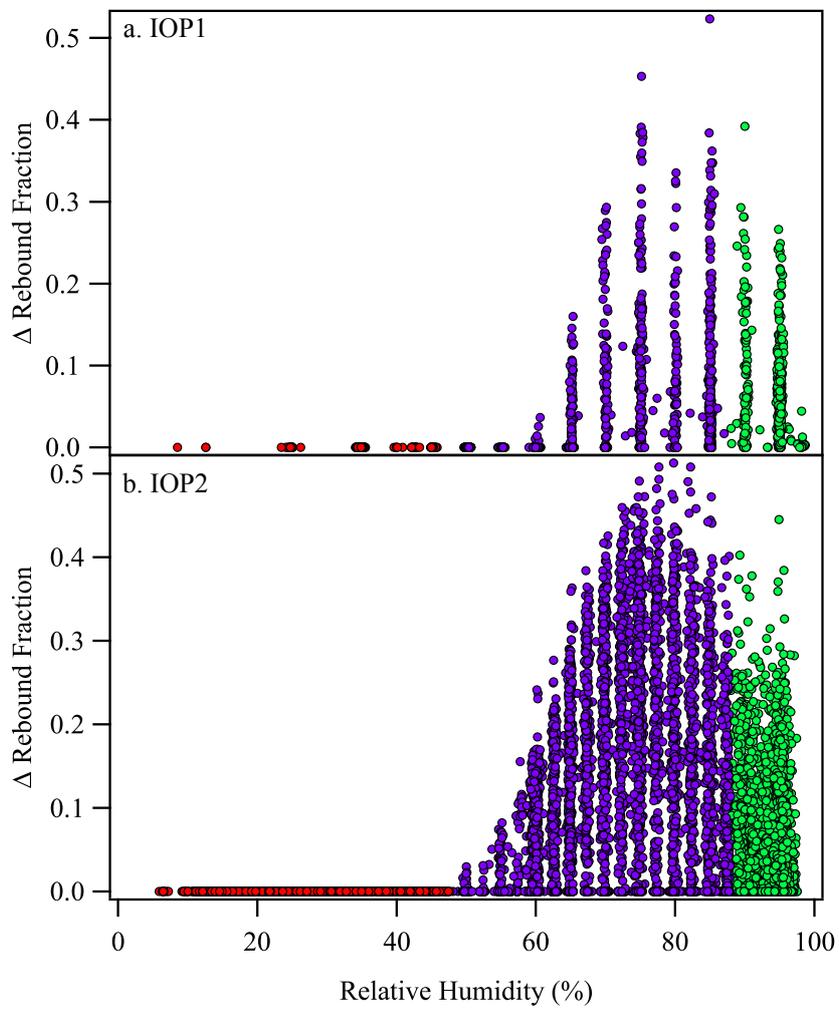


Figure 3

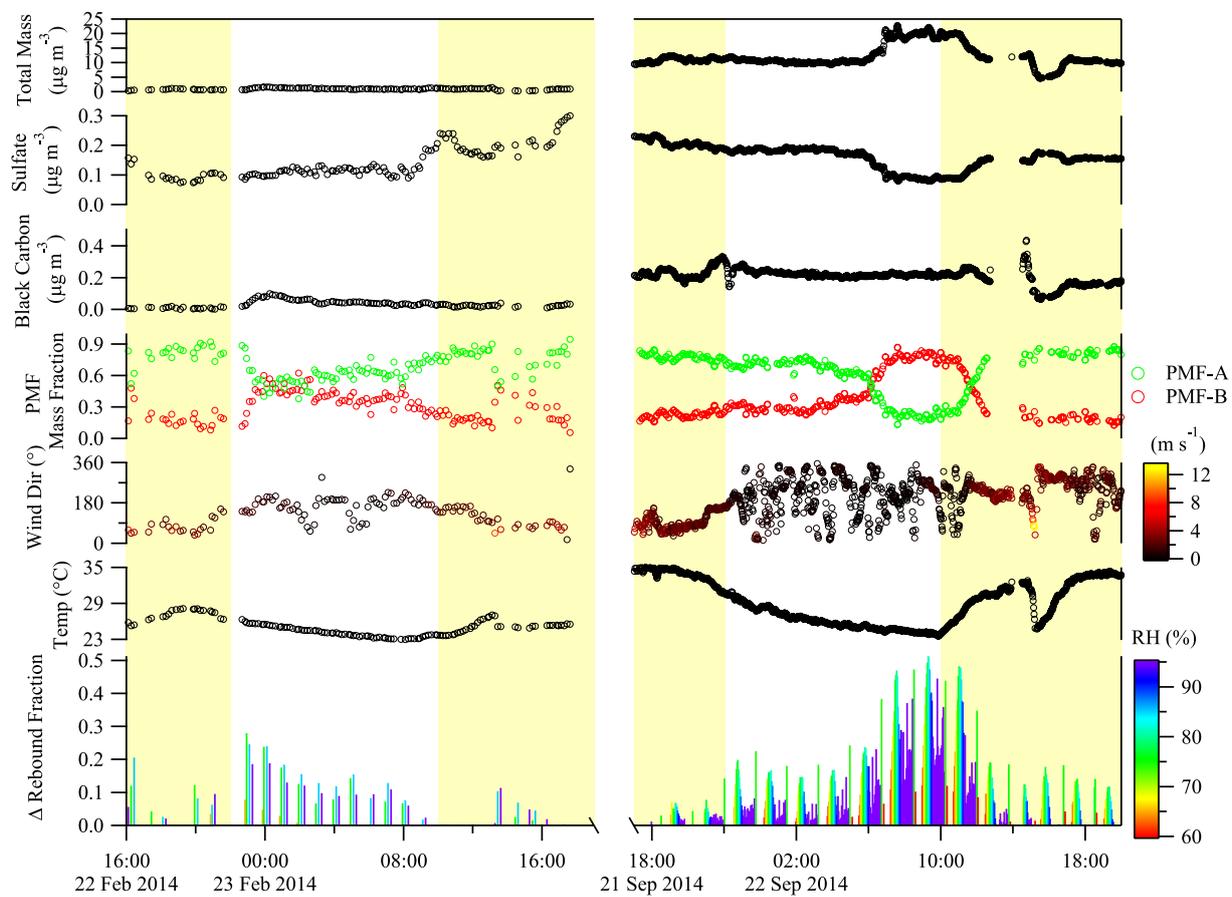


Figure 4

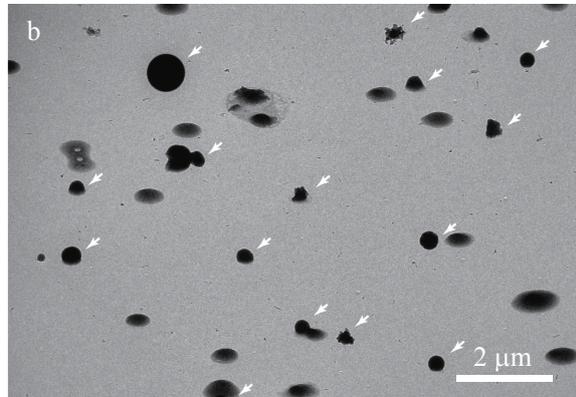
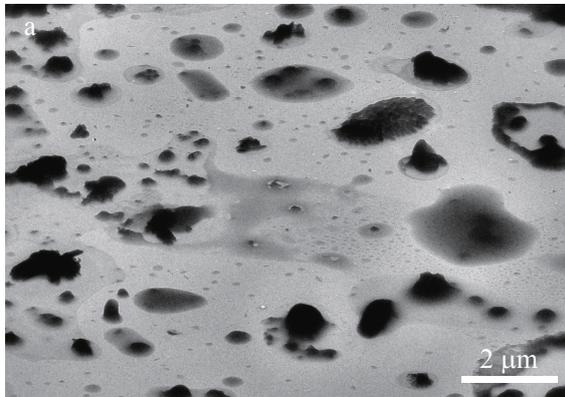


Figure 5

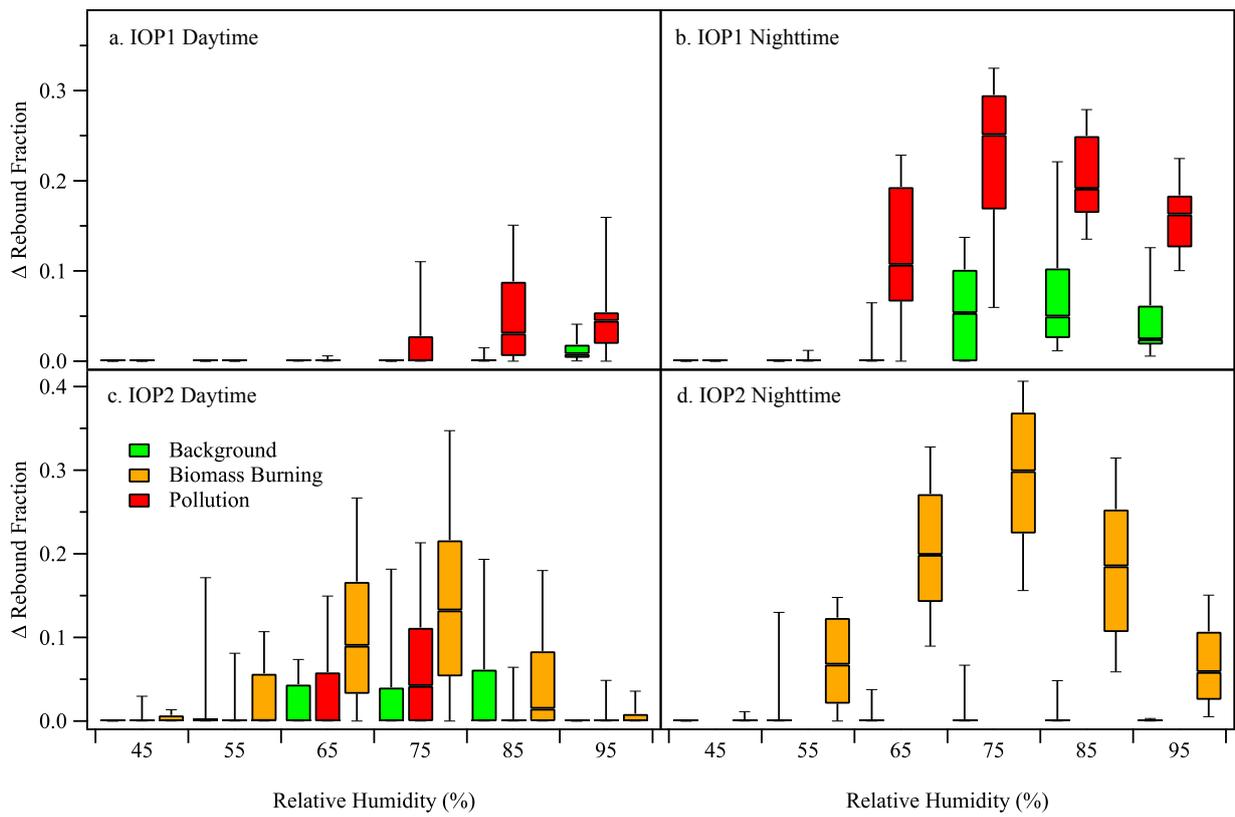


Figure 6

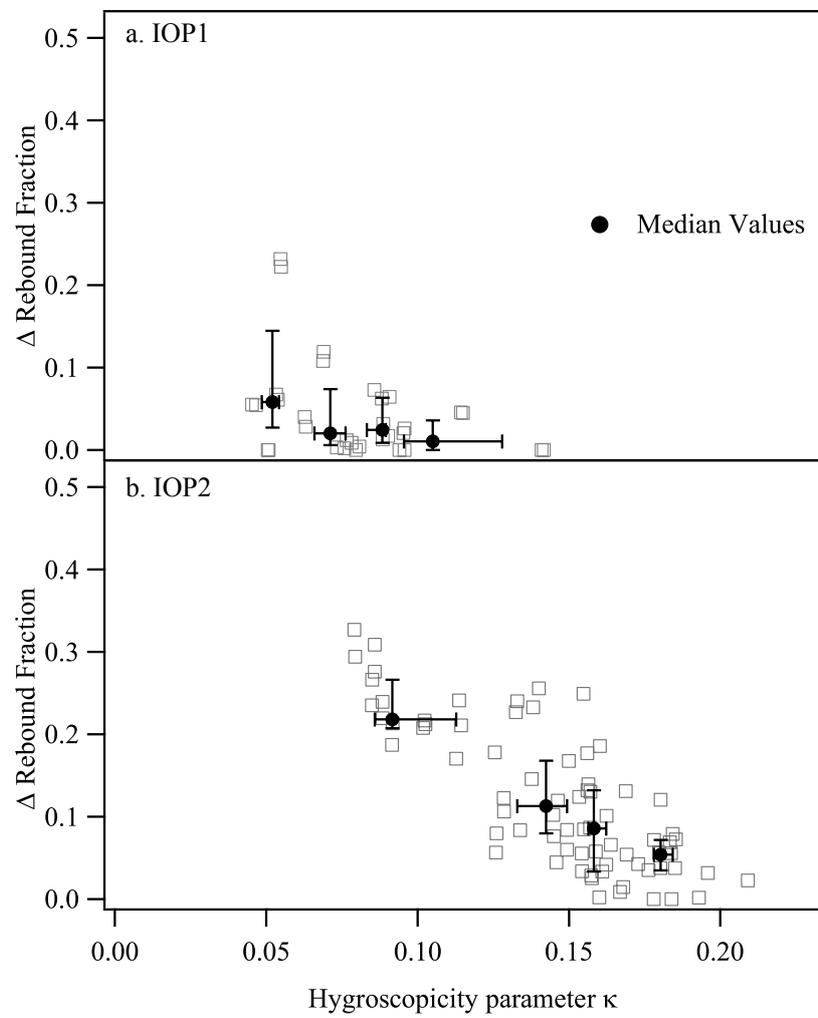


Figure 7

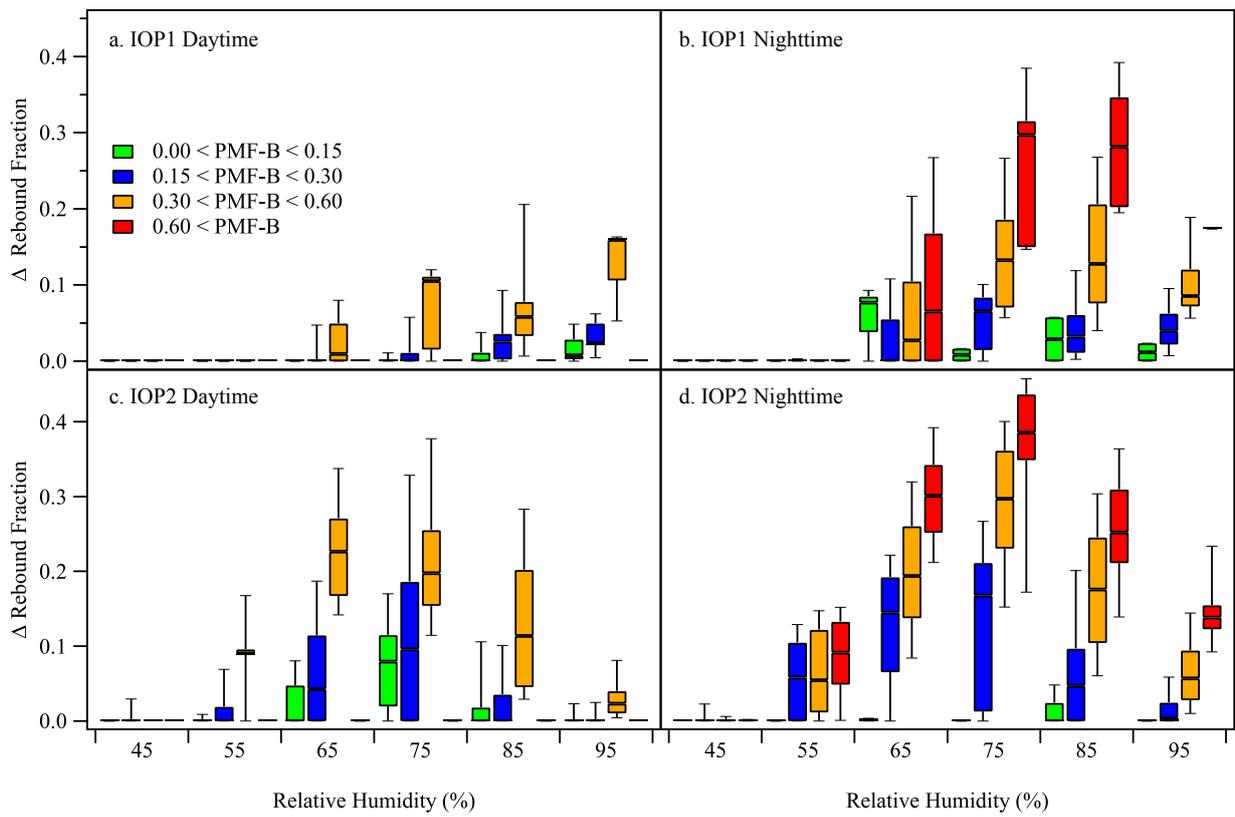


Figure 8

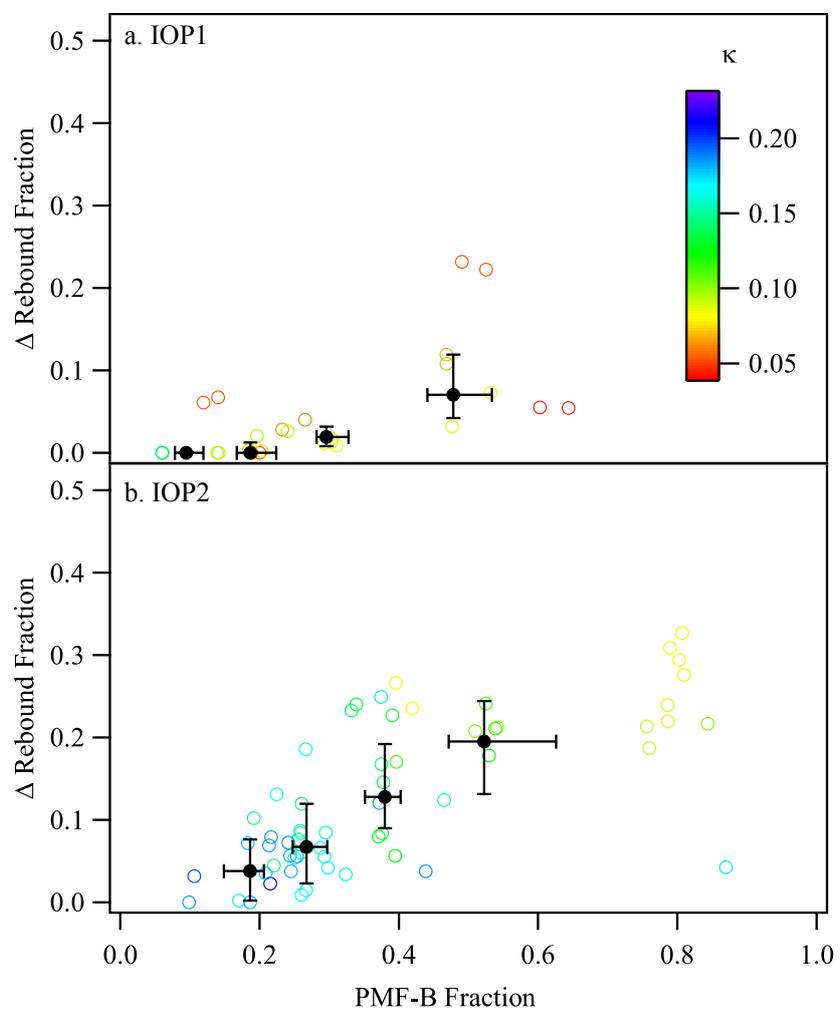


Figure 9

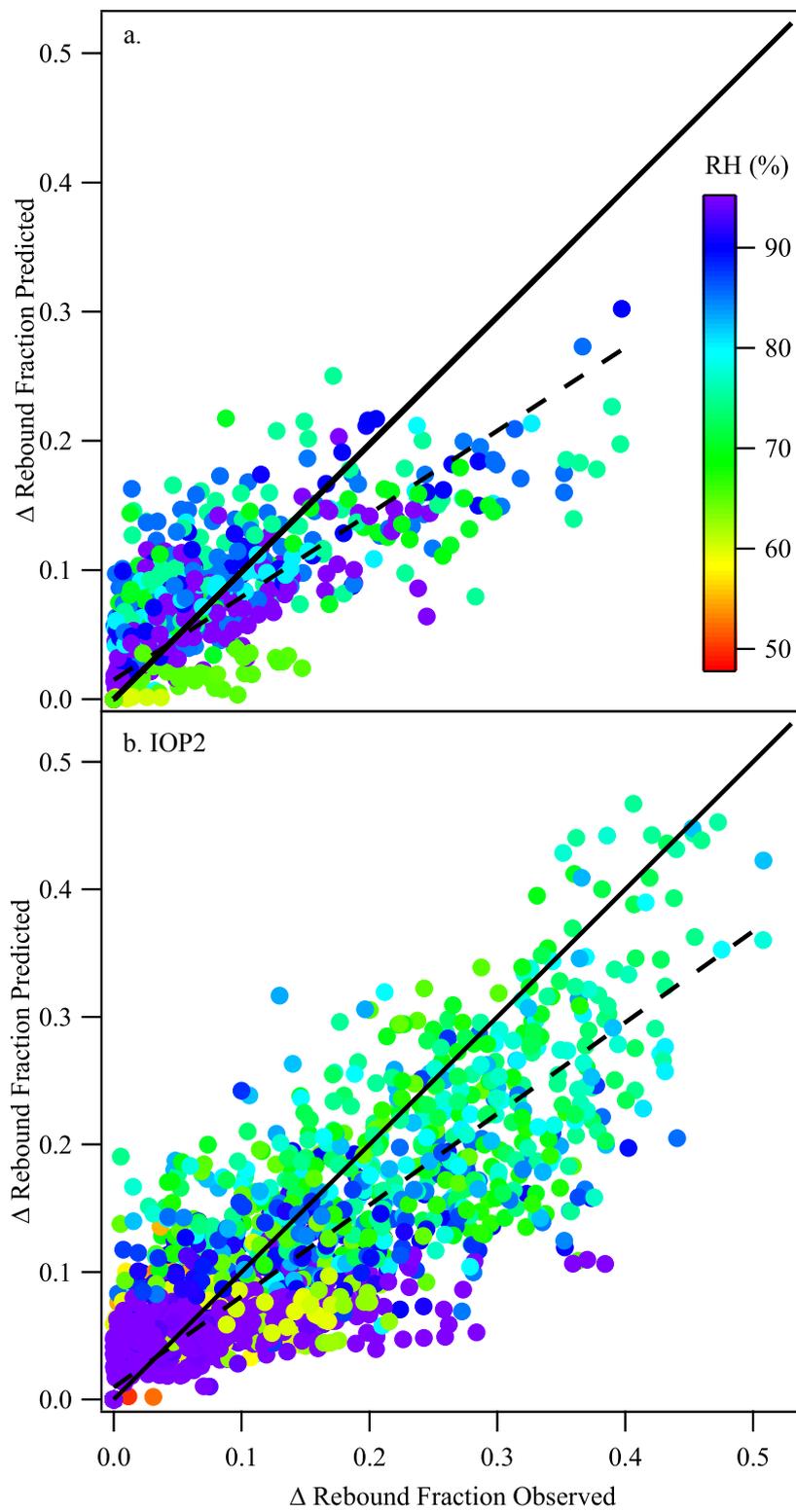


Figure 10

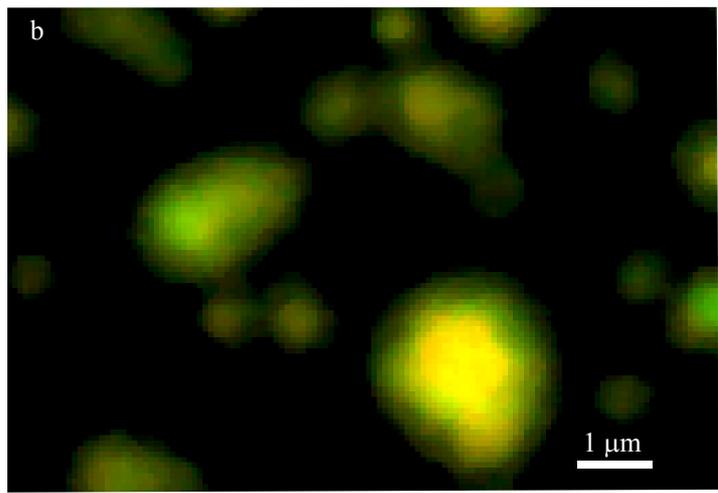
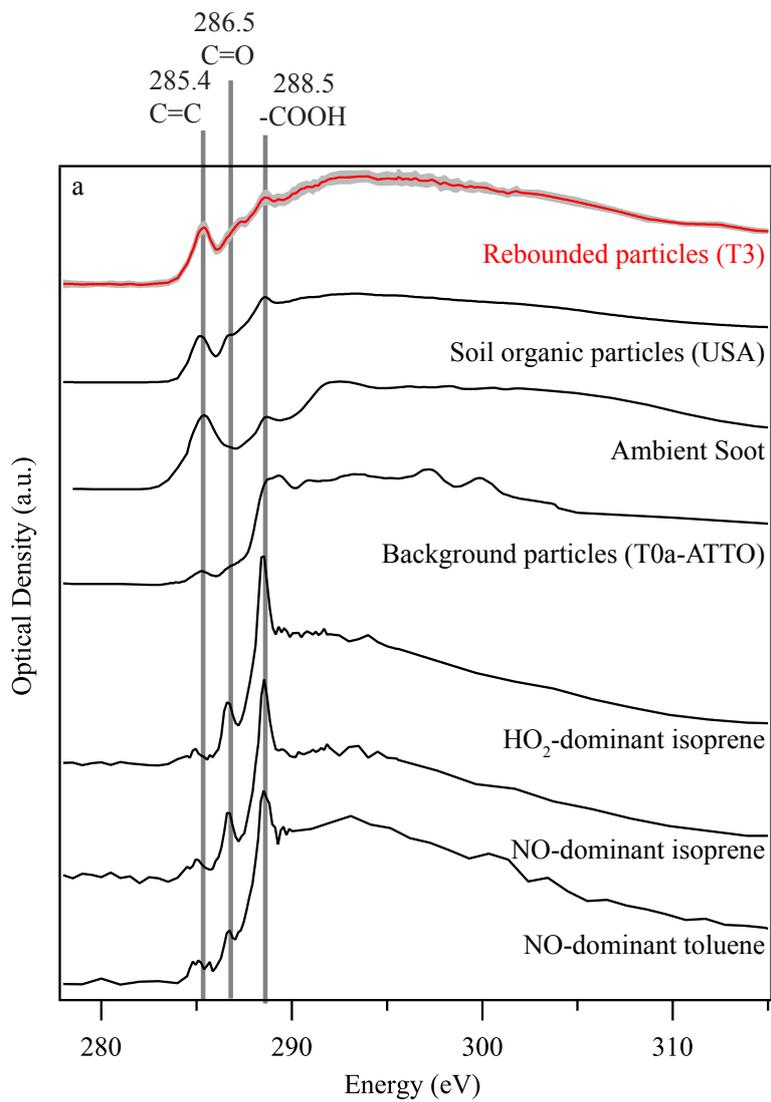


Figure 11