1289 Supplemental Information

In the main text, we noted a discrepancy between overall average aerosol volume estimates 1290 1291 based on size measurements vs. AMS for the flight analyzed here (see Figure S1). We checked 1292 to see if this bias was also present in the individual plumes studied here by calculating the 1293 volume changes from the sizing instruments and the derived volume changes from the 1294 AMS+rBC mass. There is guite a bit of scatter in the volume enhancements, with most of the 1295 points falling along the same line as the data for this flight. It is unclear why the two types of 1296 volume measurements disagree more for this flight. Therefore, the bias in volume changes 1297 introduces additional uncertainty in the magnitude of the plume enhancements. 1298



1299 1300 Figure S1. Aerosol volume measured using the total aerosol mass from the AMS plus refractory 1301 black carbon (rBC) and mass-weighted densities versus the aerosol volume measured by optical size with the UHSAS after correcting for AMS lens transmission. The procedure for 1302 1303 calculating the mass-weighted density is described by Bahreini et al. [65]. On average, the 1304 measured aerosol volume from composition is roughly equal to the measured aerosol volume 1305 from size for the entire SENEX study (left hand panel) and is higher than one for the flight 1306 analyzed here (July 2, 2013, right hand panel). 1307

1308 **Corrections for AMS UMR nitrate data and applicability to pRONO**₂ **estimation** 1309

1310 Nitrate in the AMS is guantified in unit mass resolution mode (UMR) as the sum of the estimated 1311 NO⁺ at m/z 30 and NO₂⁺ at m/z 46, with a correction factor to account for the smaller ions (N⁺ and HNO₃⁺, mostly) produced from nitrate [83]. The default AMS UMR quantification algorithm 1312 1313 (documented in the AMS "fragmentation table") estimates NO⁺ as the total signal at m/z 30 minus a small (2.2% of OA at m/z 29, "Org29" in AMS parlance) subtraction to account for 1314 organic interferences and an isotopic correction for naturally-occurring ¹⁵N₂ from nitrogen in air. 1315 The default UMR fragmentation table was developed for mixed ambient aerosols, in particular in 1316 1317 urban studies, and it is the responsibility of each AMS user to correct it as needed for each 1318 study. In environments with high biogenic contributions to total OA, and/or low total nitrate 1319 concentrations, the contribution of the CH_2O^+ ion can be much larger than the default

1320 subtraction at m/z 30. Similarly, the $CH_2O_2^+$ ion at m/z 46 becomes non-negligible, and hence 1321 nitrate reported from AMS data with UMR resolution will frequently be overestimated in these 1322 situations. The poor performance of the default AMS correction is likely due to the initial focus 1323 on urban OA with high nitrate fractions when deriving those corrections [83, 84].

1324

Here we derive a set of corrections based on an aircraft high-resolution (HR) dataset acquired 1325 with the University of Colorado HR-AMS [85] on the NASA DC-8 during the SEAC⁴RS campaign 1326 1327 [86]. SEAC⁴RS took place with a strong emphasis on the SEUS 6 weeks after the SENEX flight 1328 analyzed in this manuscript. Based on an initial screening of the correlations of the CH_2O^+ and 1329 $CH_2O_2^+$ ions with UMR signals, 10 potential UMR m/z between m/z 29 and m/z 53 were selected as viable for deriving suitable corrections. Further analysis using three specific 1330 SEAC⁴RS flights (RF11 on 30 Aug 30th, 2013, RF16 on Sep 11th, 2013 and RF18 on Sep 16th, 1331 2013) that covered a wide range of OA composition with both strong biogenic contributions and 1332 1333 fresh and aged biomass plumes showed that only four m/z (29, 42, 43 and 45) had good 1334 enough S/N and robust enough correlations to be used as corrections. Table S1 summarizes 1335 the correction coefficients obtained in this analysis, and Figure S2 shows the ability of matching 1336 the actual NO⁺ and NO₂⁺ signals (as obtained from high-resolution analysis of these flights) with 1337 the corrected UMR procedure. These corrections are applied as:

- 1338
- 1339 1340

UMR NO = Signal(m/z30) – a_i*Signal(Variable_i) UMR NO₂ = Signal(m/z 46) – b_i*Signal(Variable_i)

1341

1342 with the coefficients a_i and b_i as reported in Table S1. It should be noted that in all cases the 1343 contributions of $C^{18}O^+$ to m/z 30 need to be subtracted first before applying the correction (which 1344 is constrained to the organic CO_2^+ signal, measured at m/z 44, by the naturally-occurring 1345 isotopic ratio and assuming that OA produces $CO^{+} = CO_{2}^{+}$ [87, 88]. Likewise, the contribution of 1346 ¹³CO⁺ to Org29 needs to be subtracted first. It is hence very important for this analysis that the 1347 corrections to the AMS frag table to suitably estimate the contribution of gas phase CO_2^+ to total UMR m/z 44 as well as the baseline correction for m/z 29 be properly applied first [83]. Finally, 1348 1349 also note that the corrections using m/z 29 and 43 are rather based on Org29 and Org43, which 1350 are standard AMS products that take the OA relative ionization efficiency (RIE) into account. 1351

1352For the SEAC⁴RS dataset, the corrections amounted to on average subtracting 55% from UMR1353m/z 30 and 33% from UMR m/z 46. Despite this large subtraction, the corrected data correlates1354very well with the HR AMS results, with less than 5% deviation in the regression slope between1355the two datasets.

1356

1357 Although all of the corrections in Table S1 were valid for the SEAC⁴RS data set, for the flight 1358 analyzed here we chose Org29 to correct *m/z* 30 and *mz* 45 correction to correct *m/z* 46 1359 because they were the closest organic signals to the UMR nitrate peaks with organic 1360 interferences and may be more valid for other field studies where different types of OA are 1361 sampled. After these UMR signals were corrected and the appropriate RIEs and CE were 1362 applied, the nitrate mass concentrations in the final data archive for the flight analyzed here 1363 were reduced by 0-0.24 µg sm⁻³, averaging 0.11 µg sm⁻³ or 32%. The corresponding increase in 1364 OA due to the organic interferences in the UMR nitrate had linear dependence on the reported 1365 OA mass concentrations ($r^2 = 0.89$) with a slope of 1.3%.

1366

To estimate the fraction of nitrate that is organic nitrate (pRONO₂) the use of the NO₂⁺/NO⁺ ratio 1367 1368 with an empirically determined pRONO₂ calibration ratio has been successfully used previously with HR-AMS data [33, 36-38, 47, 67, 89]. Figure S2 summarizes how well the ratio of the 1369 corrected UMR m/z 30 and 46 signals correlate with the NO₂⁺ and NO⁺ (and ratios) determined 1370 1371 using HR data. As expected, there is considerable scatter at very low nitrate concentrations 1372 (which is a considerable part of the dataset, as the time series shows, since the free 1373 troposphere was sampled extensively). However, for the predicted pRONO₂ (which is massweighted), most of this scatter disappears, and for concentrations above 0.1 µg sm⁻³ of nitrate 1374 there is good agreement between the HR results and the UMR-corrected pRONO₂, regardless 1375 1376 of the correction chosen. For lower concentrations the scatter is considerable larger, with the 1377 Org29 correction providing the best overall agreement. Based on the variability in this dataset 1378 for this correction (Org29), we estimate the uncertainty in pRONO₂ fraction apportionment using 1379 UMR to be about 30%, in addition to an estimated uncertainty for the apportionment method 1380 using HR of 20% [67]. From the comparison of UMR-corrected total nitrate to HR nitrate (not 1381 shown), we estimate an additional error of 5% for total nitrate error using these corrections. 1382

1383 As mentioned in the main text, the empirically determined pRONO₂ calibration ratio used for the 1384 flight data analyzed here was the ratio of NO₂⁺/NO⁺ from the ammonium nitrate calibration 1385 aerosols divided by 2.8. This factor was representative of multiple data sets analyzed by Day et al. [67]. The ammonium nitrate NO_2^+/NO^+ ratio was obtained from the two calibrations on 30 1386 June and 7 July that bracketed the flight on 2 July, as described above. This ratio averaged 1387 1388 0.490. Hence, the organic nitrate NO_2^+/NO^+ ratio was estimated to be 0.175. The ratio of 1389 NO_2^+/NO^+ from the flight data was then used with the pRONO₂ and ammonium nitrate NO_2^+/NO^+ 1390 calibration ratios to estimate the fraction of the total corrected nitrate mass concentrations that 1391 was organic (pRONO₂) or inorganic (nitrate associated with ammonium or NH₄NO₃). 1392 Propagating the 30% UMR vs HR uncertainty and 20% apportionment (see above) error on top 1393 of the 34% AMS total nitrate measurement uncertainty results in ±50% uncertainties in the 1394 derived organic nitrate mass concentrations (and similar for NH₄NO₃; however it will depend on 1395 the relative contributions of pRONO₂ and NH₄NO₃ to total nitrate since the absolute 1396 concentration errors associated with pRONO₂ - NH₄NO₃ apportionment should be similar [64]). 1397



1398

Figure S2. (a and b) Comparison of m/z 30 and 46 with the NO⁺ and NO₂⁺ signals from the high 1399 1400 resolution analysis of the AMS data before and after applying the four different corrections listed in Table S1. The Pearson r² for the corrected dataset is shown as well. (c) Comparison of the 1401 1402 NO_2^+/NO^+ ratio obtained from HR analysis with the ratios of the corrected UMR NO and NO_2^- 1403 variables (d) Comparison of the pRONO₂ concentrations derived using the HR and UMR NO₂⁺/ 1404 NO⁺ ratios using the method discussed in Day et al [67]. (e) Time series of the total and 1405 speciated nitrate as reported from HR analysis of the SEAC⁴RS data [90], compared to the 1406 speciation using the Org29 correction (note the logarithmic scale). The bottom time series 1407 shows the NO₂⁺/NO⁺ ratio that the speciation is based on, again for the HR and corrected UMR 1408 case.

1409 **Table S1.** Coefficients used to correct *m/z* 30 and 46 to estimate total nitrate.

AMS	Correction coefficient for	Correction coefficient for <i>m/z</i>
Variable	<i>m/z</i> 30 (a _i)	46 (b _i)
Org29	0.215	0.037
<i>m/z</i> 42	0.51	0.092
Org43	0.215	0.037
<i>m/z</i> 45	0.72	0.127





1414 text but using model NO_2 and O_3 data. Time since sunset on the x-axis is the model elapsed 1415 time (i.e., run time of the model during darkness).

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Figure S4. SOA molar yield is positively correlated with estimated plume age. This SOA molar
 yield is based on Eq. 3, with error bars determined by propagation of observed variability in
 pRONO₂ and isoprene, where multiple point averaging was possible. Markers correspond to

- plume numbers.). Based on the box model described in more detail below, the first-generation
 isoprene products peak at a approximately 4 hours plume age and then begin to decay.

Table S2. Peak ambient (wet) aerosol surface area during each plume used in the yield
analysis (plume numbers 1 – 9), and for the two longer urban plumes transected at the end of
the flight.

plume number	7/2/13 plume time (UTC)	Peak aerosol surface area (μm² cm⁻³)		
1	2:18	280		
2	2:20	370		
3	2:21	470		
4	3:03	340		
5	3:55	800		
6	4:34	470		
7	4:37	370		
8	4:39	420		
9	5:04	490		
Urban plume	5:36	340		
Urban plume	6:37	300		





Figure S5. In-plume change in sulfate mass concentration vs. change in ammonium aerosol 1433 1434 mass concentration is generally well correlated, with a slope of 5.4. The masses of the cations 1435 and anions would give an ion balance for pure $(NH_4)_2SO_4$ of $MW(SO_4)/(2 \times MW(NH_4)) = 2.7$, and for $(NH_4)HSO_4$ of $MW(SO_4)/(MW(NH_4)) = 5.4$. Hence, this slope provides support for a mix of 1436 1437 these two ammonium sulfate salts, with sometimes exclusively $(NH_4)HSO_4$. This is consistent 1438 with incomplete neutralization of the sulfate mass by ammonium. The one clear outlier (sulfate increase of 6 µg m⁻³ for Plume #5) suggests excess sulfate, rendering ammonium or other 1439 inorganic nitrate formation even less likely. Points with ammonium aerosol below 0.1 μ g m⁻³ are 1440 1441 within the variability of that measurement; their omission does not change the slope. 1442 1443

1444 Additional AMS and auxiliary data from plumes

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1446 **Table S3.** Additional information for the list of plumes used in this NO_3 + isoprene SOA yield

1447 analysis, for which key yield-related data is presented in Table 1. For each plume, the delta-

1448 values listed indicate the difference between in-plume and outside-plume background in

1449 average observed concentration. After each plume number, the numbers of points averaged for

isoprene and AMS, respectively, are listed. Plume numbers annotated with * indicate brief 1450 1451 plumes for which only single-point measurements of in-plume aerosol composition were possible.

1452

plume number [#isop/#AMS]	7/2/13 plume time (UTC)	∆ORG _{aero} (µg m ⁻³)	ΔNH _{4,aero} (µg m ⁻³)	ΔSO _{4,aero} (µg m ⁻³)	Temp (C)	%RH	lsop:MT Mole Ratio
Typical variability (µg m ⁻³):		0.75	0.1	0.5			
1 [2/3]	2:18	0.35	0	0	23.6	66.5	36.5
2 [*]	2:20	0.89	0.3	1.91	23.6	65	71.4
3 [4/5]	2:21	1.25	1.05	5.14	23.6	65.2	16.6
4 [*]	3:03	0.16	0.08	0.7	21.2	68.1	50.6
5 [3/4]	3:55	0.32	0.26	6.07	21.9	65.5	34.2
6 [2/2]	4:34	0.57	0.3	1.12	19.9	74.6	17.3
7 [5/6]	4:37	1.05	0.22	0.65	19.7	76.2	14.2
8 [2/3]	4:39	1.26	0.44	1.18	18.3	82.2	11.0
9 [7/8]	5:04	1.45	0.35	1.9	17.2	84.8	17.8

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1456 **Box model calculations**

1457 Box model simulations were performed using the Dynamically Simple Model of Atmospheric 1458 Chemical Complexity (DSMACC, http://wiki.seas.harvard.edu/geos-

chem/index.php/DSMACC_chemical_box_model), containing the Master Chemical Mechanism 1459

1460 v3.3.1 chemistry scheme (http://mcm.leeds.ac.uk/MCM/). The model approach is similar to that

1461 described in detail in Edwards et al. 2017, and the accompanying supplement, with the model 1462 run over a 9.5 hour night to simulate the nocturnal residual layer. For the nocturnal simulation

1463 used in this work (for both the plume lifetime calculation and the peroxy radical lifetime analysis

- 1464 in Sect. 4.3) the model was initialized with concentrations of the constraining species
- representative of the SENEX observations (Table S4). As the model is simulating power plant
- 1466 plume evolution from point of emission, a starting NO mixing ratio of 10 ppb was used to
- 1467 constrain NO_x, and the chemistry scheme was subsequently allowed to partition the reactive 1468 nitrogen. The top panels in Figure S7 show the evolution of key species during this nocturnal
- 1469 simulation.
- 1470 **Table S4**: Species constrained (MCM v3.3.1 names) during model simulations and constraining
- 1471 values. Constraint column indicates if species concentrations were held at the constrained value
- 1472 throughout the simulation (Fixed) or allowed to vary after initialization (Initial).

Species	Species Mixing ratio		Constraint	
NO	9.28	ppb	Initial	
03	55.72	ppb	Initial	
CO	134.00	ppb	Fixed	
CH4	1920.00	ppb	Fixed	
C5H8	2606.80	ppt	Initial	
APINENE	38.87	ppt	Initial	
BPINENE	195.50	ppt	Initial	
LIMONENE	12.42	ppt	Initial	
MACR	454.13	ppt	Initial	
MVK	1006.00	ppt	Initial	
IC4H10	47.00	ppt	Fixed	
NC4H10	128.00	ppt	Fixed	
C2H6	1199.00	ppt	Fixed	
C2H4	117.00	ppt	Fixed	
C2H2	145.00	ppt	Fixed	
NC6H14	20.00	ppt	Fixed	
IC5H12	120.00	ppt	Fixed	
NC5H12	76.00	ppt	Fixed	
C3H8	344.00	ppt	Fixed	
C3H6	26.00	ppt	Fixed	
CH3COCH3	2556.00	ppt	Fixed	
BENZENE	35.90	ppt	Fixed	
C2H5OH	2239.00	ppt	Fixed	
MEK	309.00	ppt	Fixed	
CH3OH	5560.00	ppt	Fixed	

1473 The daytime simulation used for comparison in Sect. 4.3 of the main manuscript (lower panels

1474 of Figure S7) uses the same initialization as the nocturnal simulation; with the only difference

being the model is run during the daytime. Photolysis rates are calculated using TUV

1476 (https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model).

1477 The daytime simulation does not accurately simulate daytime mixing ratios of species such as

1478 O₃ representative of SENEX observations. However, the intent of this simulation is to compare 1479 model daytime peroxy radical fate and lifetime with the nocturnal simulation. The presence of

1480 intense convective mixing in the daytime planetary boundary layer of the Southeast US makes

accurately modeling these concentrations difficult with a zero dimensional model.



1483

1484 Fig. S6. Model calculated NO, NO₂, O₃, and isoprene (left) and NO₃, N₂O₅ and OH (right for the nocturnal (top) and daytime (bottom) simulations shown in Sect. 4.3. 1485

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Additional considerations investigated via RO₂ fate box modeling 1488

1489 Based on the potentially larger than previously estimated contribution of RO₂+RO₂ reactions at 1490 night, we considered a related possible source of a high bias in the determined SOA yields. If 1491 NO₃ reaction with the major daytime isoprene oxidation products MVK and/or MACR produces RO₂ radicals that can cross-react with NO₃ + isoprene products to produce condensable 1492 1493 products, this would be a mechanism of recruiting isoprene-derived organic mass into the 1494 aerosol, but that original isoprene oxidation would not be counted in the denominator of the yield 1495 calculation, since its interaction with NO₃ began as MACR or MVK. In the box model, substantial 1496 MVK and MACR are available in the plume at nighttime, but only MACR reacts with NO₃, and a 1497 maximum fraction of one-guarter of MVK+MACR losses go to reaction with NO₃ overnight (see 1498 Figure S8). In addition, in our power plant plume observations, MVK+MACR are not observed to 1499 be appreciably depleted by the large NO_3 injection, further suggesting that this chemistry is not 1500 a substantial additional source of SOA (see Figure S9).



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Figure S7. Calculated (via MCM) loss rate contributions for the daytime isoprene products methyl vinyl ketone (MVK) and methacrolein (MACR) in the simulated nighttime plume used in the text. Only MACR reacts with NO₃, and the contribution of this process to total losses (green stack) is relatively minor.



Figure S8. MVK and MACR are not titrated on the timescale of these yield estimates in powerplant plumes.

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