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2 **Fossil vs. non-fossil CO sources in the US: New airborne constraints from ACT-**  
3 **America and GEM**  
4

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22 **Key Points:**

- 23
- 24 • We interpret an ensemble of airborne measurements with the GEOS-Chem model to  
25 constrain US fossil fuel and non-fossil CO sources
  - 26 • Measurements reveal an approximate 30% overestimate of US fossil fuel CO emissions  
27 in the National Emissions Inventory
  - 28 • During summer regional fossil fuel sources account for just 9-16% of total boundary  
29 layer CO over eastern North America  
30

**31 Abstract**

32 Carbon monoxide (CO) is an ozone precursor, oxidant sink, and widely-used pollution tracer.  
33 The importance of anthropogenic versus other CO sources in the US is uncertain. Here we  
34 interpret extensive airborne measurements with an atmospheric model to constrain US fossil and  
35 non-fossil CO sources. Measurements reveal a low bias in the simulated CO background and a  
36 30% overestimate of US fossil CO emissions in the 2016 National Emissions Inventory. After  
37 optimization we apply the model for source partitioning. During summer, regional fossil sources  
38 account for just 9-16% of the sampled boundary layer CO, and 32-38% of the North American  
39 enhancement—complicating use of CO as a fossil fuel tracer. The remainder predominantly  
40 reflects biogenic hydrocarbon oxidation plus fires. Fossil sources account for less domain-wide  
41 spatial variability at this time than non-fossil and background contributions. The regional fossil  
42 contribution rises in other seasons, and drives ambient variability downwind of urban areas.

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**45 Plain Language Summary**

46 Carbon monoxide (CO) is an air pollutant that is emitted from fossil fuel combustion and from  
47 forest and agricultural fires. CO is also produced in the atmosphere through the oxidation of  
48 hydrocarbons from both natural and human-caused sources. US fossil fuel CO emissions have  
49 been declining in recent years, and their current importance relative to other regional sources is  
50 uncertain. Here, we interpreted a large group of aircraft-based CO measurements with a high-  
51 resolution atmospheric model to better quantify US fossil and non-fossil fuel CO sources over  
52 the eastern half of the US. We find that US fossil fuel CO emissions in the 2016 National  
53 Emissions Inventory are overestimated by approximately 30%. Furthermore, during summer  
54 regional fossil fuel sources account for only a small fraction of the CO over North America  
55 compared to the background concentrations already present in air entering North America, and  
56 compared to the regional source from natural hydrocarbon oxidation. This complicates the use of  
57 CO as a tracer for estimating fossil fuel sources of other pollutants such as carbon dioxide.

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## 67 **1 Introduction**

68 Carbon monoxide (CO) is the largest sink of atmospheric hydroxyl (OH) radicals  
69 (Müller et al., 2018) and a major tropospheric ozone precursor (Hu et al., 2017). It is emitted  
70 from fossil fuel and biomass combustion and is also indirectly produced from the oxidation of  
71 methane and non-methane volatile organic compounds (VOCs). CO removal occurs mainly via  
72 reaction with OH, forming atmospheric carbon dioxide (CO<sub>2</sub>) at an annual rate equivalent to  
73 ~10% of the global fossil fuel source (Duncan et al., 2007; Friedlingstein et al., 2019). As a  
74 result of its oxidative effects and their feedbacks, CO has a global warming potential  
75 approximately 5× that of CO<sub>2</sub> on a 100-year timescale (Shindell et al., 2009).

76 According to the National Emissions Inventory Collaborative (NEIC) Emissions  
77 Modeling Platform, based on the US Environmental Protection Agency (EPA) National  
78 Emissions Inventory (NEI), US CO emissions totaled ~55 Tg in 2016, with fossil fuel and  
79 biomass burning emissions accounting for 41 Tg and 14 Tg, respectively (NEIC, 2019). Fossil  
80 fuel sources in the inventory are predominantly mobile (on-road: 18 Tg; non-road: 10 Tg) and in  
81 the case of on-road emissions, mainly (90%) due to non-diesel light-duty vehicles. Gasoline  
82 combustion similarly accounts for the majority (80%) of the estimated non-road mobile source  
83 (NEI, 2014). Annual fossil fuel CO emissions in the NEI decreased by approximately 50 Tg/year  
84 from 2000-2016, driven by a nearly 70% drop in the estimated mobile source (EPA, 2019).

85 CO has traditionally been used as a fossil fuel tracer to diagnose anthropogenic sources of  
86 CO<sub>2</sub> and other species (e.g., Cheng et al., 2018; Halliday et al., 2019; Nathan et al., 2018; Super  
87 et al., 2017). In the US, however, the dramatic decline in transportation-related emissions  
88 (Gaubert et al., 2017; NEI, 2018; Parrish, 2006) means that non-fossil fuel CO sources are  
89 increasingly important. For example, Hudman et al. (2008) estimated that VOC oxidation  
90 (predominantly from biogenic precursors) was a two-fold larger CO source than direct  
91 combustion emissions over the US during summer 2004. Furthermore, previous NEI versions  
92 have been shown to overestimate US anthropogenic CO emissions by as much as 60% (Fujita et  
93 al., 2012; Kim et al., 2013; Salmon et al., 2018; Brioude et al., 2011; Brioude et al., 2013; Plant  
94 et al., 2019), so the non-fossil fuel CO fraction may be even greater than suggested by current  
95 inventories.

96 Together, the large recent emission trends and demonstrated inventory biases imply  
97 significant uncertainty in the current CO budget over North America. Two airborne measurement  
98 campaigns conducted from 2016-2019 with widespread, multi-seasonal coverage over the  
99 eastern half of the US provide new constraints for addressing this issue: the Atmospheric Carbon  
100 and Transport (ACT)-America mission, with 5 dual-aircraft deployments across three US regions  
101 (Davis et al., 2021), and the Greenhouse Emissions in the Midwest (GEM) mission with 3  
102 deployments across the US Upper Midwest (Yu et al., 2020; 2021). Here, we employ the GEOS-  
103 Chem chemical transport model (CTM) to interpret these datasets in terms of their implications  
104 for fossil fuel versus non-fossil and primary versus secondary CO sources over the US.

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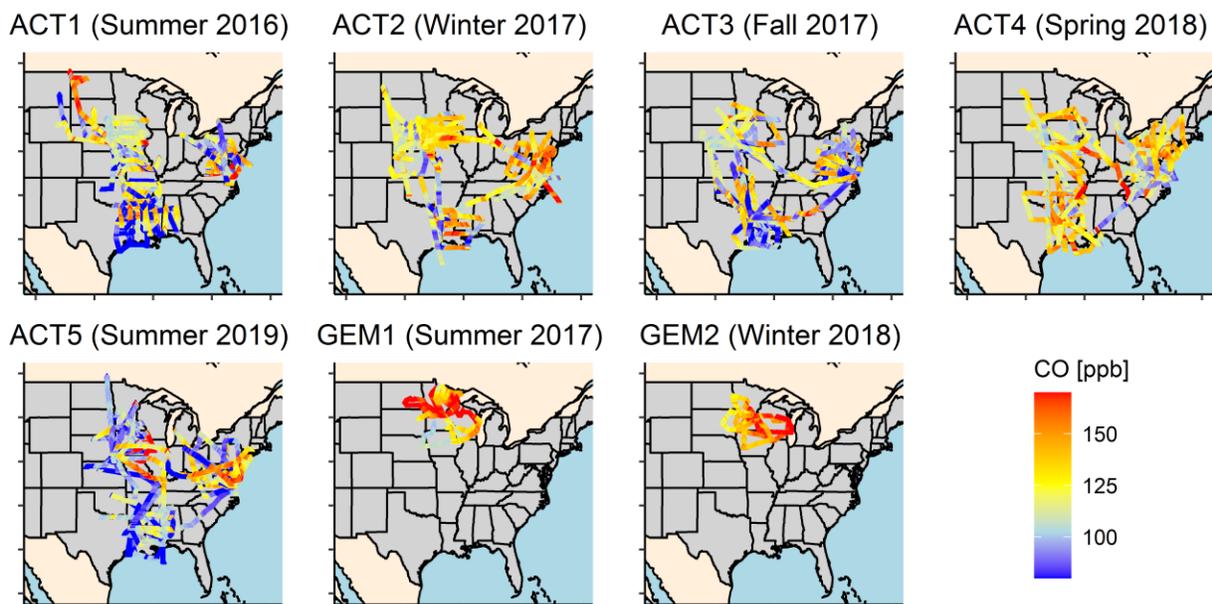
106 **2 Methods**

## 107 2.1 Aircraft Measurements

108 Figure 1 shows flight-tracks for the ACT-America and GEM airborne deployments used  
109 here. ACT-America took place during summer 2016 (ACT1; see Table S1), winter 2017 (ACT2),  
110 fall 2017 (ACT3), spring 2018 (ACT4), and summer 2019 (ACT5) (Davis et al., 2018; Davis et  
111 al., 2021). Each deployment featured measurements aboard two aircraft (C-130 Hercules: 487  
112 flight hours; Beechcraft B200 King Air: 513 flight hours) across the US Midwest, Northeast, and  
113 South. Sampling altitudes ranged from 0.1-8.7 km above ground level (AGL); only data below 8  
114 km AGL are employed here. Airborne CO measurements were also performed for the first two  
115 GEM campaigns over the US Upper Midwest during summer 2017 (GEM1) and winter 2018  
116 (GEM2). Measurements took place on a Mooney aircraft (76 flight hours) from 0.1 to 2.2 km  
117 AGL (Yu et al., 2020; Yu et al. 2021). We employ data from ACT1-ACT4 for CO source  
118 estimation and reserve ACT5, GEM1 and GEM2 for independent evaluation of the results.

119 ACT-America CO dry-air mole fraction measurements used here were performed in-situ  
120 by wavelength-scanned cavity ring-down spectroscopy (CRDS; Picarro G2401-m) with  $\pm 5$  ppb  
121 estimated uncertainty (DiGangi et al., 2021; Wei et al., 2021). Additional CO measurements  
122 were obtained during ACT-America via air samples collected on-board both aircraft with  
123 Programmable Flask Packages (PFP) (Baier et al., 2020; Wei 2021; Davis et al., 2018). An  
124 intercomparison of the C-130-H and B-200 Picarro datasets using the PFP observations as  
125 transfer standard shows no significant difference (Figure S1) and we treat them here as a single  
126 statistical ensemble. GEM CO measurements were performed by continuous-wave tunable  
127 infrared laser absorption spectrometry (Aerodyne CW-TILDAS) with  $\pm 1$  ppb estimated  
128 uncertainty (Gvakharia et al., 2018; Millet et al., 2019). In-situ measurements for ACT and GEM  
129 were made at 0.4 Hz and we use 1-minute averaged data in analyses that follow.

130 We also employ airborne CO measurement over the remote Pacific from the Atmospheric  
131 Tomography Mission (ATom) (Wofsy et al., 2018) to evaluate and adjust the chemical boundary  
132 conditions used in the nested GEOS-Chem simulations (Section 2.2). ATom featured pole-to-  
133 pole sampling from 0.2-12 km altitude during four separate deployments; CO measurements  
134 used here were collected using the NOAA Picarro instrument with estimated  $\pm 3.6$  ppb  
135 uncertainty (Chen et al., 2013 ). ATom1 (Northern Hemisphere summer 2016), ATom2 (winter  
136 2017), ATom3 (fall 2017) and ATom4 (spring 2018) overlap temporally with ACT1-ACT4,  
137 respectively, and are applied for correction accordingly. ATom1 data is further used for ACT5  
138 and GEM1 background correction, and ATom2 data for GEM2 background correction, given  
139 their matching seasonal coverage. Correction procedures are explained below. All datasets are  
140 calibrated on the WMO X2014A scale.



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142 Figure 1: ACT-America and GEM flight-tracks colored by observed CO mixing ratios.

## 143 2.2 GEOS-Chem Simulations

144 We interpret the above airborne datasets using a GEOS-Chem (v12.6.3;  
145 doi:10.5281/zenodo.3552959) simulation nested at  $0.25^\circ \times 0.3125^\circ$  (latitude  $\times$  longitude)  
146 resolution over North America ( $60^\circ$ - $130^\circ$ W,  $9.75^\circ$ - $60^\circ$ N) with 47 vertical layers (Figure S2).  
147 Model runs are driven by GEOS-FP meteorological data from NASA GMAO (Lucchesi, 2013),  
148 and employ timesteps of 10-min (transport, convection) and 20-min (emissions, chemistry). A 1-  
149 month nested spinup is used for initialization.

150 Chemical boundary conditions (3-hourly) for the nested model domain are obtained from  
151 global simulations at  $2^\circ \times 2.5^\circ$  and bias-corrected using a latitude-dependent fit of model-  
152 measurement 0.1 quantile differences ( $6^\circ$  latitude bins from  $66^\circ$ S- $54^\circ$ N) along the ATom flight-  
153 tracks over the remote Pacific (Figure S3). As described later, we also perform a sensitivity  
154 analysis without this boundary condition correction as one test of our results.

155 We use tagged tracers (Fisher et al., 2017) to track contributions to ambient CO from  
156 direct and indirect CO sources within the North American domain shown in Figure S2 and from  
157 the chemical boundary conditions ( $CO_{bc}$ ). Tagged direct sources include US on-road mobile  
158 emissions ( $CO_{usrd}$ ), US non-road mobile emissions ( $CO_{usnr}$ ), other US anthropogenic sources  
159 ( $CO_{usot}$ ), non-US anthropogenic emissions ( $CO_{camx}$ ; from Canada and Mexico) and wildfires  
160 plus agricultural burning ( $CO_{bb}$ ). We separately track secondary CO ( $CO_{prod}$ ) from the oxidation  
161 of biogenic VOCs ( $CO_{prod_{bio}}$ ), anthropogenic VOCs ( $CO_{prod_{anth}}$ ), and other precursors  
162 ( $CO_{prod_{oth}}$ ; methane plus pyrogenic VOCs) occurring within the North American domain. CO  
163 production and removal rates are computed using archived fields from full-chemistry simulations  
164 at  $2^\circ \times 2.5^\circ$ ; secondary contributions from biogenic and anthropogenic VOCs are derived from  
165 runs with the corresponding emissions perturbed by 10%.

166 Global anthropogenic emissions in the model are from the Community Emissions Data  
167 System (Hoesly et al., 2018) overwritten for the US by the 2016 EPA NEI (NEIC2016v1; NEIC,  
168 2019) and for Canada by the Air Pollutant Emission Inventory (APEI, 2020). Biogenic emissions  
169 are from the Model of Emissions of Gases and Aerosols from Nature (MEGANv2.1)

170 implemented as described by Hu et al. (2015), and biomass burning emissions use the Quick-Fire  
171 Emissions Dataset (Koster et al., 2015).

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### 173 **3 Results**

#### 174 3.1 Measured Versus Predicted CO over the Eastern and Central US

175 Figure 2a-g shows the mean vertical CO profiles measured during ACT1-ACT5 and  
176 GEM1-GEM2. Average concentrations during the ACT-America flights peak in the planetary  
177 boundary layer (PBL; defined here as  $z < 2$  km) at ~120-125 ppb during summer and fall, and at  
178 ~140 ppb during spring and winter. Concentrations during GEM (which sampled farther north  
179 and predominantly within the PBL) are slightly higher. Aloft, we see free tropospheric ( $z > 4$  km)  
180 concentrations ranging seasonally between ~80-90 ppb (summer) and ~100-110 ppb (winter).

181 Also shown in Figure 2a-g are the CO mixing ratios simulated by GEOS-Chem along the  
182 flight-tracks at the time of measurement, with the corresponding tagged-tracer source  
183 contributions. The base-case simulation successfully captures the relative vertical distribution of  
184 CO, but underestimates its abundance in all seasons except fall (ACT3). The magnitude of this  
185 low bias during spring, summer, and winter ranges from 9 ppb (averaged below 2 km) during  
186 spring for ACT4 to 48 ppb during summer for GEM1.

187 Transport from outside North America makes the largest contribution to ambient CO over  
188 the eastern half of the US in the GEOS-Chem base-case simulation (Figure 2a-g). This  
189 background varies little with altitude and changes seasonally in concert with the CO lifetime,  
190 from ~50 ppb in summer (for ACT1 and ACT5) to ~100 ppb in winter (for ACT2 and GEM2).  
191 We see from Figure 2 that the background contribution dominates total CO in the free  
192 troposphere (71-96% above 4 km, lowest in summer). At lower altitudes, regional CO sources  
193 play a larger role; nevertheless, the CO background still represents 55% (summer) to 78%  
194 (winter) of the total averaged model abundance below 2 km.

195 Figure 2h-n shows the base-case model partitioning of North American CO  
196 enhancements (i.e., excluding  $CO_{bc}$ , which is already present in air entering North America)  
197 during ACT-America and GEM. The regional secondary source is further partitioned into  
198 biogenic, anthropogenic, and other (methane + pyrogenic VOC) contributions. We see that  
199 secondary production accounts for a significant fraction of the predicted North American CO  
200 source, particularly during summer when, in the case of ACT1 and ACT5, it mainly arises from  
201 biogenic VOC oxidation. Primary emissions mainly reflect US anthropogenic sources (in turn  
202 dominated by on-road and off-road mobile emissions). GEM1, over the Upper Midwest, featured  
203 a larger contribution from biomass burning.

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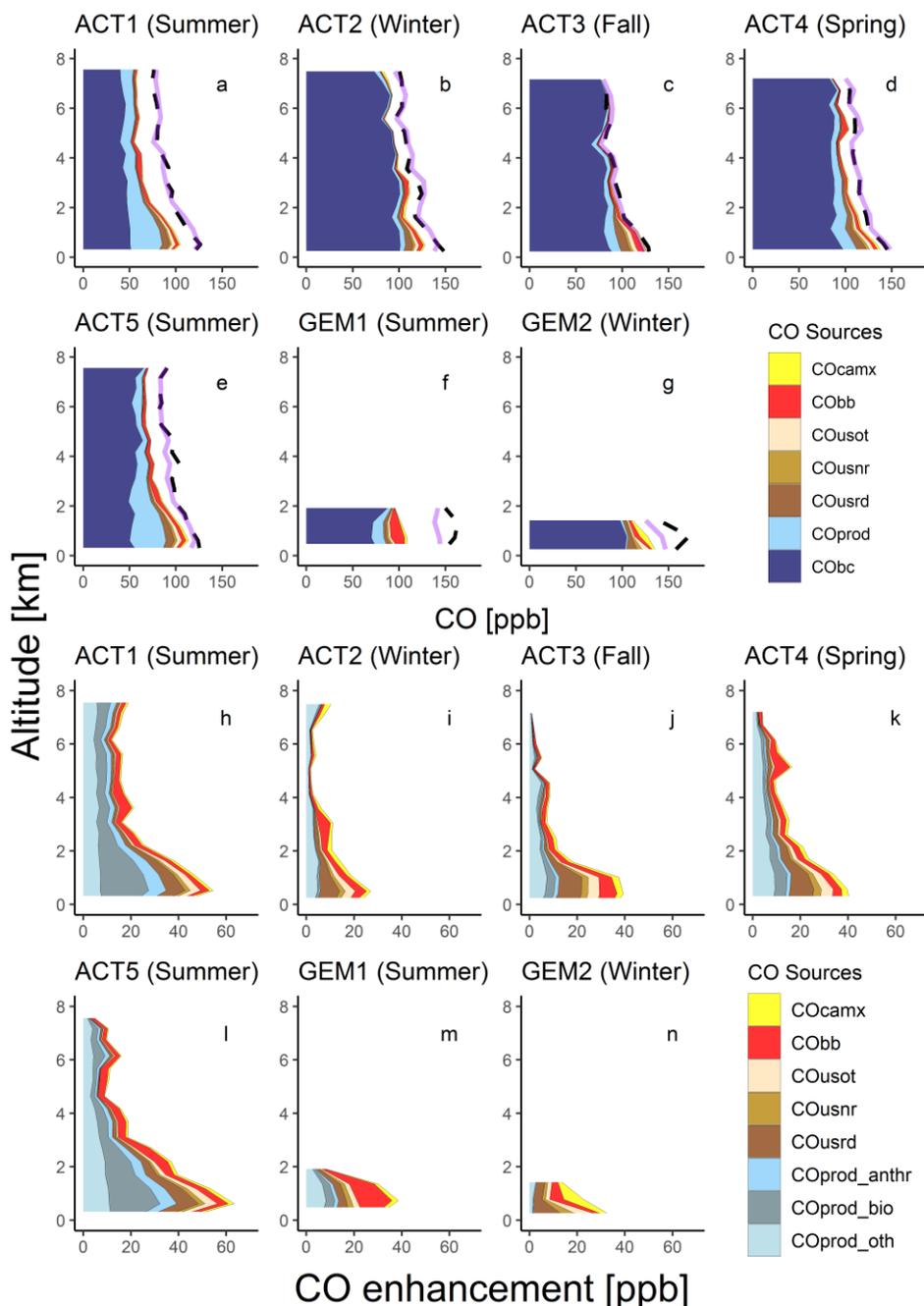
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212 Figure 2: Mean CO profiles during ACT-America and GEM. Panels a-g compare observed CO  
 213 mixing ratios (black dashed lines) with those predicted by the prior GEOS-Chem simulation  
 214 (stacked color plots). Pink lines show simulated CO concentrations after source optimization.  
 215 Panels h-n show the above-background source contributions based on the prior GEOS-Chem  
 216 simulation.  $CO_{usrd}$ ,  $CO_{usnr}$ ,  $CO_{usot}$ : anthropogenic CO from US on-road, non-road, and other  
 217 sources.  $CO_{camx}$ : anthropogenic CO emitted in Canada + Mexico.  $CO_{bb}$ : CO from North  
 218 American biomass burning.  $CO_{prod}$ : CO photochemically produced over North America from  
 219 the oxidation of biogenic VOCs ( $CO_{prod\_bio}$ ), anthropogenic VOCs ( $CO_{prod\_anthr}$ ), and methane  
 220 + biomass burning VOCs ( $CO_{prod\_oth}$ ).  $CO_{bc}$ : CO transported from outside North America.

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## 222 3.2 CO Source Optimization

223 We next apply the base-case tagged tracer simulations discussed above to develop  
224 improved US CO source estimates based on the ACT-America observations. The optimization is  
225 performed separately for ACT1-ACT4 and consists of two steps. First, since background CO  
226 dominates the total free tropospheric abundance (Figure 2), we attribute the prior model bias  
227 aloft accordingly and correct the simulated  $CO_{bc}$  based on the mean >4 km model-measurement  
228 differences for each campaign. Given the vertical uniformity of  $CO_{bc}$  this correction is applied  
229 throughout the column and ranges from a factor of 1.0 during fall to 1.5 during summer.

230 Second, after subtracting this corrected background we derive top-down adjustments on  
231 regional CO sources by regressing the model tagged tracers against the observed above-  
232 background enhancements below 2 km AGL. Selected tracers are grouped for optimization to  
233 avoid multicollinearity and based on their relative abundance. During summer we thus optimize  
234 1) direct CO emissions from US onroad, non-road mobile, and other anthropogenic sources  
235 ( $CO_{usnei} = CO_{usrd} + CO_{usnr} + CO_{usot}$ ) and 2) regional secondary CO production from biogenic  
236 and anthropogenic VOCs ( $CO_{prod_voc} = CO_{prod_bio} + CO_{prod_anth}$ ) as single variables based on  
237 the high cross-correlation ( $R = 0.92-0.98$ ) among the grouped tracers. Other secondary  
238 production ( $CO_{prod_oth}$ ) is not optimized as it is primarily from methane and implicitly corrected  
239 by the preceding background adjustment. CO sources from Canada and Mexico and from  
240 biomass burning each make up <18% of the above-background model abundance during ACT1-4  
241 and are likewise not optimized. During other seasons the same procedure is used but without  
242 optimizing  $CO_{prod_voc}$  as it then accounts for <16% of the mean above-background  
243 enhancements. A sensitivity test described later explores how the choice of tracer groups for  
244 optimization affects our results.

245 In this way we obtain seasonal top-down correction factors for the NEIC2016v1 US  
246 anthropogenic CO emissions, along with a top-down correction to the regional secondary source  
247 from biogenic + anthropogenic VOCs during summer. Results shown in Table 1 are consistent  
248 across the seasonal ACT-America campaigns in revealing a moderate NEI overestimate of US  
249 anthropogenic CO emissions, with coefficients ranging from  $0.66 \pm 0.05$  to  $0.79 \pm 0.03$  (here and  
250 below, stated uncertainties reflect bootstrapped 95% confident intervals). We find that secondary  
251 CO production from regional VOC oxidation is well-represented in the model, with a derived  
252 scale factor of  $0.91 \pm 0.03$ .

253 Figure 2 and Table 1 show that the optimization successfully minimizes the prior model  
254 bias, and either improves or maintains the prior model:measurement correlation. An exception is  
255 ACT3, where the prior simulation was already essentially unbiased (< 3 ppb) with high  
256 correlation. However, the posterior fit quality here is still comparable to that obtained in other  
257 seasons. In the following section, we apply a series of statistical and sensitivity analyses and  
258 independent data comparisons to further test the representativeness and robustness of these  
259 results.

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266 Table 1. Seasonal CO source optimization<sup>1</sup>

	$CO_{usnei}$		$CO_{prod.voc}$		Intercept	VIF <sup>2</sup>	Mean bias (ppb)		RMSE <sup>3</sup> (ppb)		R	
	Scale factor	Mean (ppb)	Scale factor	Mean (ppb)			Prior	Post	Prior	Post	Prior	Post
ACT1 (summer)	0.66 ± 0.05	13.2	0.91 ± 0.03	25.4	-0.2 ± 0.3	3.1	17.6	-0.2	26.4	16.5	0.75	0.81
ACT2 (winter)	0.79 ± 0.03	12.77			1.8 ± 0.3		14.8	1.7	21.4	15.5	0.69	0.69
ACT3 (fall)	0.69 ± 0.03	16.77			5.5 ± 0.5		2.5	5.5	13.4	14.2	0.79	0.75
ACT4 (spring)	0.74 ± 0.02	16.94			-2.7 ± 0.4		8.8	-2.6	18.1	17.0	0.65	0.62

<sup>1</sup> Stated uncertainties reflect 95% confidence intervals computed through bootstrap resampling.

<sup>2</sup> Variance inflation factor.

<sup>3</sup> Root mean square error.

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### 273 3.3 Uncertainty Analysis

274 The bootstrapped uncertainty estimates in Table 1 provide a first evaluation of the  
275 optimization results, showing that the individual scaling coefficients derived from ACT1-ACT4  
276 are each statistically robust. The similar findings across ACT1-ACT4 provide a second piece of  
277 supporting evidence, as the deployments represent four separate datasets and independent source  
278 derivations that all lead to consistent results. Third, we see from Figure 2 and Table S2 that the  
279 CO source optimization (derived from ACT1-ACT4 data) strongly improves model performance  
280 versus independent airborne data from ACT5, GEM1, and GEM2, which were not employed in  
281 the optimization.

282 As a fourth test, we perform the CO source optimization separately for the two ACT-  
283 America aircraft. Table S3 shows that we arrive at the same conclusions when analyzing the B-  
284 200 and C-130 observations independently as opposed to treating them as a combined dataset.  
285 Specifically, we infer an NEI overestimate of US anthropogenic CO emissions in both cases,  
286 with derived scale factors spanning 0.54-0.87 (sensitivity tests) versus 0.66-0.79 (base analysis).  
287 The modest adjustment to the modeled secondary CO source from regional biogenic and  
288 anthropogenic VOCs is likewise independently supported by both airborne datasets (scale factors  
289 of 0.74-0.96 versus 0.91 in the base-case).

290 A fifth evaluation repeats the base-case optimization with alternate boundary conditions  
291 ( $CO_{bc}$ ) for the nested model domain—i.e., employing the native model output for this purpose  
292 and omitting the ATom-based background adjustment (Section 2.2; Figure S3). Results in Table  
293 S4 show that scale factors derived in this way are statistically consistent with the base-case  
294 analysis. For a sixth and final test, we modify the tracer groupings used for optimization and  
295 instead derive ACT1-ACT4 scale factors for 1)  $CO_{usnei}$  and 2) the sum of all other regional  
296 source tracers. Results shown in Table S5 are again consistent with the base-case findings, with a  
297 slightly wider range for the  $CO_{usnei}$  scale factor (0.58-0.85) and a modestly degraded  
298 observational fit.

299 Overall, the above uncertainty tests all support our core findings, and we proceed to  
300 interpret the optimized results in terms of their implications for fossil fuel versus non-fossil, and  
301 primary versus secondary, CO sources over the US.

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## 303 3.3.3 Optimized CO Source Contributions

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305 Figure 3a-g shows the optimized primary and secondary North American contributions to  
306 ambient CO as sampled during ACT-America and GEM. We find that secondary production  
307 (mainly from biogenic VOCs) is the dominant summertime North American CO source for air  
308 masses sampled by ACT-America, accounting for ~70% of the total PBL enhancement.  
309 Secondary production is also significant at other times (e.g., 26-45% of the PBL enhancement  
310 during the fall, winter, and spring ACT-America campaigns) but then mainly reflects regional  
311 methane oxidation along with pyrogenic VOC oxidation. To the north, the importance of  
312 secondary CO over the Upper Midwest during GEM is significantly less (~7-40%)—reflecting  
313 lower biogenic VOC emissions and slower regional photochemistry. In total, photochemical CO  
314 sources contribute between 2 ppb (winter; GEM2) and 31 ppb (summer; ACT5) to the average  
315 sampled PBL enhancements, versus 13-25 ppb from primary emissions.

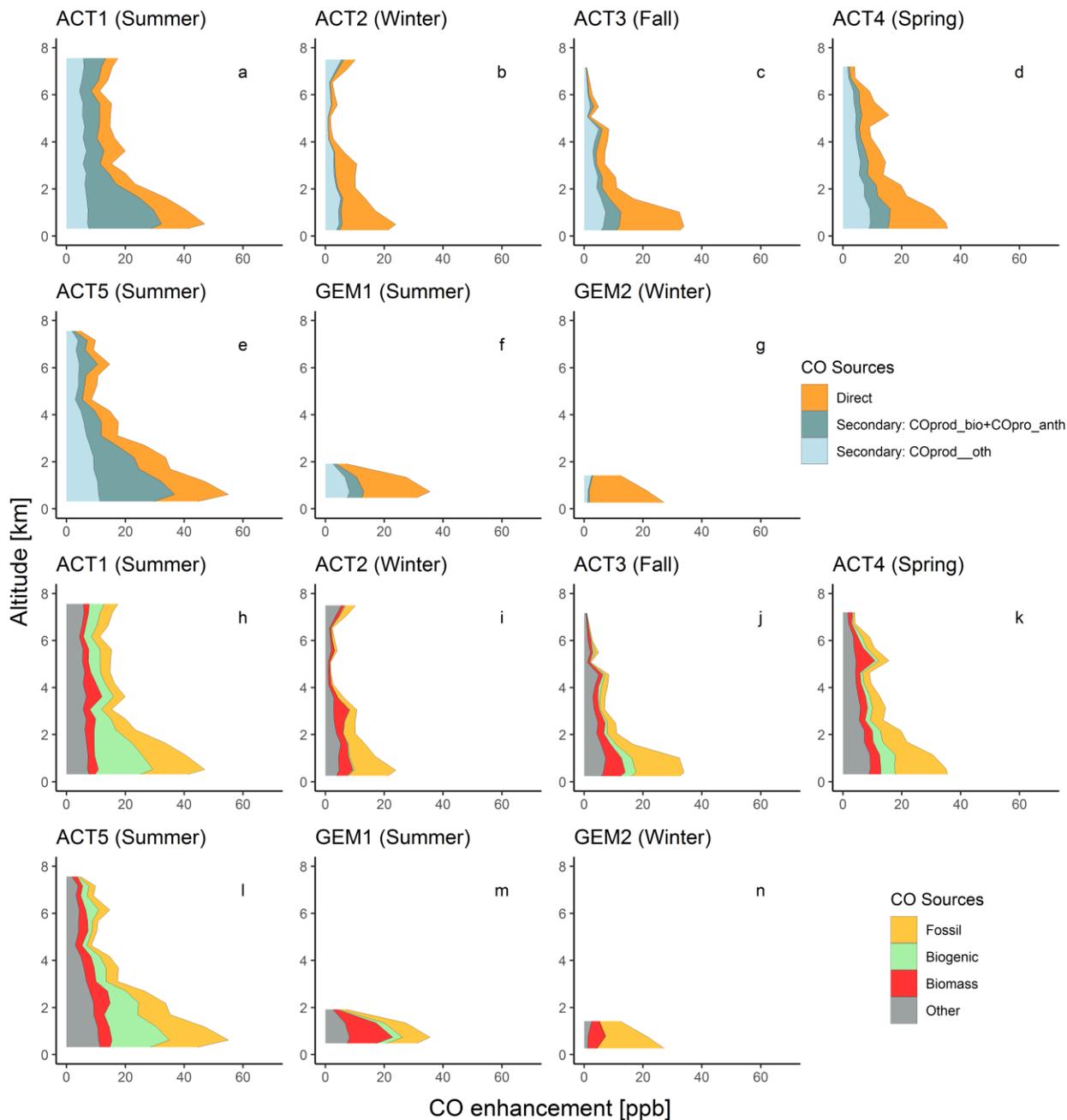
316 In Figure 3h-n we further partition the optimized CO abundance into fossil fuel versus  
317 non-fossil contributions. Here, fossil fuel sources include primary emissions plus secondary  
318 production from anthropogenic VOC, while non-fossil fuel sources include biogenic VOC  
319 oxidation plus biomass burning CO emissions. The remainder is from the oxidation of methane  
320 and of fire-derived VOCs. Results show that fossil fuel sources account for just 32-38% of the  
321 North American PBL CO enhancements sampled by ACT-America and GEM during summer,  
322 increasing to 48-49% during spring/fall and 57-84% during winter.

323 The findings above reveal the complications of using CO as an anthropogenic tracer,  
324 particularly during summer—as fossil fuel sources account for just 9-16% of the total PBL  
325 abundance, and 32-38% of the North American enhancement, during this season. However, for  
326 many applications (e.g., applying species:species correlations for source partitioning), source  
327 impacts on tracer variability can be more important than their absolute magnitude. For example,  
328 one might expect the secondary CO source to be relatively diffuse and that direct anthropogenic  
329 emissions would be a more important driver of ambient CO variability over the US.

330 To explore this expectation, Figures S4-S5 show the CO standard deviation by source  
331 category (based on the optimized GEOS-Chem simulation), for each airborne campaign in its  
332 entirety. In the summertime PBL sampled by ACT-America and GEM, the CO variability due to  
333 North American (primary + secondary) fossil fuel sources is substantially smaller (7-10 ppb)  
334 than that associated with background (15-21 ppb) and regional non-fossil fuel (11-15 ppb)  
335 contributions. In other seasons, regional fossil fuel emissions drive as much or more of the CO  
336 variability than non-fossil sources, but (except in the case of GEM) this variability is still smaller  
337 than that associated with the CO background.

338 The characterization above, treating each ACT-America and GEM campaign as a single  
339 statistical dataset, mainly describes spatial patterns of CO variability across the eastern half of  
340 the US as a whole. If we instead apply the optimized model to map the drivers of temporal CO  
341 variability (Figures S6-S10), we observe in all seasons a dominant role for fossil fuel emissions  
342 in and downwind of most urbanized areas. A similar finding applies for fires in specific affected  
343 regions. Temporal variability associated with secondary CO, manifesting most strongly in  
344 summer, is relatively low over much of the US Southeast where precursor VOC emissions are  
345 highest but is elevated around the periphery of this region (e.g., Figures S6, S11, S16). We  
346 attribute this to transport-driven effects at the edges of a large and diffuse source region (Figures  
347 S11-S15). In other seasons, temporal variability associated with secondary CO is small, with

348 fossil fuel emissions, biomass burning, and background CO playing more important roles (Figure  
 349 S7-S9).  
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 353 Figure 3: Observationally-constrained CO source attribution over the eastern US. Plotted are the  
 354 mean above-background CO profiles from the optimized GEOS-Chem simulation along the  
 355 aircraft flight-tracks. Panels a-g partition the regional CO enhancements into direct and  
 356 secondary components. Direct sources include: anthropogenic CO from US on-road (CO<sub>usrd</sub>),  
 357 non-road (CO<sub>usnr</sub>), and other sources (CO<sub>usot</sub>), anthropogenic CO emitted in Canada + Mexico  
 358 (CO<sub>camx</sub>), and biomass burning CO (CO<sub>bb</sub>). Secondary sources (CO<sub>prod</sub>) include oxidation of

359 biogenic + anthropogenic VOC ( $\text{CO}_{\text{prod\_bio}} + \text{CO}_{\text{prod\_anth}}$ ) and of methane + biomass burning  
360 VOCs ( $\text{CO}_{\text{prod\_oth}}$ ). Panels h-n partition the regional CO enhancements into fossil fuel (direct +  
361 secondary), biogenic (exclusively secondary), biomass burning (direct), and other (mainly  
362 methane oxidation, plus secondary biomass burning) contributions.  
363

#### 364 4 Conclusions

365 We applied measurements from 13 airborne campaigns to develop new constraints on CO  
366 sources over the central and eastern US. Data were collected over 1,000 flight hours across all  
367 seasons, representing the densest airborne dataset yet for CO source quantification over North  
368 America. Campaign-average PBL (< 2 km) mixing ratios ranged from 121 (summer) to 158 ppb  
369 (winter). Interpreting this dataset with a high-resolution version of the GEOS-Chem CTM driven  
370 by the US EPA's NEIC2016v1 inventory, we find that the model accurately captures the  
371 observed CO vertical profile shape but underestimates its abundance (by 9-48 ppb) in all seasons  
372 except fall. This disparity partly reflects a bias in the model CO background, and after correction  
373 we infer an NEI overestimate of fossil fuel CO emissions, with a derived top-down adjustment  
374 factor of 0.72 (0.54-0.87; best estimate and uncertainty range across all sensitivity tests and  
375 seasons). For comparison, the US EPA estimates that national fossil fuel CO emissions  
376 decreased by 8% from 2016-2019 (EPA, 2019). Our top-down estimate for the secondary CO  
377 source from North American VOC emissions agrees well with the prior model value, with a  
378 derived scale factor of 0.91 (0.74-0.96). If the above comparisons are nationally representative,  
379 the implied US fossil fuel CO source for 2016-2019 was 29 (22-36) Tg/y, compared to the prior  
380 NEIC2016v1 estimate of 41 Tg/y (for 2016).

381 After optimizing the model based on the airborne constraints, we find that the CO  
382 background represents on average 55-78% of the PBL CO sampled during the aircraft  
383 campaigns. During summer, North American fossil fuel sources account for only 9-16% of the  
384 sampled PBL CO, and 32-38% of the enhancements associated with regional sources. Non-fossil  
385 sources from biogenic VOC oxidation and fires account for 40-45% of the above-background  
386 enhancements at this time, with the remainder mainly from regional methane oxidation. In other  
387 seasons, however, fossil fuel emissions are the largest regional source of CO.

388 Application of CO as a fossil fuel tracer is challenged by the fact that, during the growing  
389 season, such sources account for only a modest fraction of the CO burden and its spatial  
390 variability across the US. However, in and near most urbanized regions the temporal variability  
391 in CO is still dominated by fossil fuel sources. The number of locations where this remains the  
392 case will likely diminish, as US fossil fuel CO emissions are expected to continue declining with  
393 future vehicle emission regulations, advanced emission after-treatment technologies, and fleet  
394 electrification (Winkler et al., 2018; Nopmongcol et al., 2017).  
395

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405

406

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