Large Format Additive Manufacturing and Machining using High Melt Temperature Polymers. Part I: Real-time Particulate and Gas-phase Emissions

Aleksandr B. Stefaniak[a,*], Lauren N. Bowers[a], Stephen B. Martin, Jr[a], Duane R. Hammond[b], Jason E. Ham[a], J. R. Wells[a], Alyson R. Fortner[a], Alycia K. Knepp[a], Sonette du Preez[c], Jack R. Pretty[b], Jennifer L. Roberts[b], Johan L. du Plessis[c], Austin Schmidt[d], Matthew G. Duling[a], Andrew Bader[d], M. Abbas Virji[a]

[a] National Institute for Occupational Safety and Health, Morgantown, WV, USA, 26505 (AStefaniak@cdc.gov; LBowers@cdc.gov; SMartin1@cdc.gov; JHam1@cdc.gov; RWells@cdc.gov; AFortner@cdc.gov; AKnepp@cdc.gov; MDuling@cdc.gov; MVirji@cdc.gov)

[b] National Institute for Occupational Safety and Health, Cincinnati, OH, USA, 45213 (DHammond@cdc.gov; JPretty@cdc.gov; JLRoberts1@cdc.gov)

[c] North-West University, Occupational Hygiene and Health Research Initiative, Private Bag X6001, Potchefstroom, South Africa, 2520 (dupreezsonette@nwu.ac.za; Johan.DuPlessis@nwu.ac.za)

[d] Additive Engineering Solutions, Akron, OH, USA, 44305 (austin@additiveeng.com; andrew@additiveeng.com)

[*]Author to whom correspondence should be sent:

Aleksandr B. Stefaniak, PhD, CIH
National Institute for Occupational Safety and Health
Respiratory Health Division
1095 Willowdale Road
Morgantown, WV 26505
Tel.: +1-304-285-6302
E-mail: AStefaniak@cdc.gov

Supporting Information

Figure S1. Positioning of samplers outside of (a) LFAM-1 on the operator's platform (view is looking away from LFAM-1 toward LFAM-2) and (b) LFAM-2 mounted on a tripod at the operator's station.

Table S1. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of ABS polymer.[a]

	Job 1		Job 2		Job 3		Job 4		Job 5		Job 6	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
PID												
TVOC	1480±278 (1166 – 3211)	--	224±148 (<2.3 – 4305)	1113±2087 (<2.3 – 22067)	224±673 (<2.3 – 19286)	92±48 (<2.3 – 773)	357±69 (269 – 627)	762±142 (558 – 1232)	713±198 (404 – 1579)	291±157 (11 – 1189)	75±64 (<2.3 – 918)	77±98 (<2.3 – 1205)
Gases												
CO	0	--	0.8±0.2 (0 – 1.4)	0.01±0.03 (0 – 0.2)	0.6±0.2 (0.1 – 0.9)	0.1±0.2 (0 – 1.5)	0.001±0.01 (0 – 0.1)	0.7±0.1 (0.5 – 1.0)	0	0.6±0.1 (0.2 – 0.9)	0	0.3±0.3 (0 – 0.9)
CO_2	541±36 (472 – 786)	--	374±81 (345 – 2795)	364±6 (353 – 393)	374±16 (350 – 433)	380±21 (363 – 573)	512±4 (507 – 523)	417±4 (405 – 426)	451±18 (426 – 577)	344±10 (313 – 377)	445±14 (410 – 615)	437±11 (255 – 459)

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM

-- = No sample collected

Table S2. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of PC polymer.[a]

	Job 1		Job 2		Job 3		Job 4	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
PID								
TVOC	211±445	239±309	157±278	60±45	247±105	394±35	547±246	594±160
	(<2.3 – 6173)	(<2.3 – 2924)	(<2.3 – 2531)	(<2.3 – 328)	(57 – 783)	(340 – 457)	(92 – 1941)	(351 – 1274)
Gases								
CO	0.2±0.1	0.001±0.01	0.001±0.001	4.5±0.1	0.001±0.001	4.4±0.1	0	1.1±0.7
	(0 – 0.6)	(0 – 0.2)	(0 – 0.1)	(4.1 – 4.9)	(0 – 0.1)	(4.0 – 4.8)		(0 – 2.3)
CO_2	305±10	375±12	421±13	345±3	418±2	307±2	562±10	530±7
	(287 – 328)	(354 – 400)	(409 – 522)	(338 – 353)	(413 – 425)	(303 – 311)	(538 – 634)	(495 – 553)

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM

Table S3. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of Ultem® polymer.[a]

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
PID				
TVOC	1125±730	--	1743±868	--
	(565 – 7107)		(792 – 9097)	
Gases				
CO	0	--	0	--
CO_2	1348±198	--	1297±13	--
	(1290 – 3597)		(1263 – 1329)	

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM
-- = No sample collected

Table S4. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of PPS polymer.[a]

	Job 1*		Job 2		Job 3	
	Outside	Inside	Outside	Inside	Outside	Inside
PID						
TVOC	827±1185	1828±1641	1529±1309	2143±1477	253±529	668±998
	(37 – 8023)	(99 – 10724)	(259 – 11451)	(328 – 10630)	(21 – 6407)	(2 – 12509)
Gases						
CO	0.3±0.1	0.004±0.02	0.3±0.1	0.002±0.01	0.3±0.1	0.03±0.1
	(0 – 0.6)	(0 – 0.2)	(0 – 0.6)	(0 – 0.1)	(0 – 0.7)	(0 – 0.8)
CO_2	301±7	352±4	294±7	355±6	295±26	364±96
	(291 – 329)	(345 – 364)	(285 – 339)	(265 – 365)	(278 – 728)	(338 – 911)

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM

* Nozzle clogged during extrusion

Table S5. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of PSU polymer.[a]

	Job 1		Print 2	
	Outside	Inside	Outside	Inside
PID				
TVOC	388±1206	524±378	219±709	414±642
	(<2.3 – 14198)	(<2.3 – 2107)	(<2.3 – 18359)	(<2.3 – 4865)
Gases				
CO	0	0	0.01±0.04	0
			(0 – 1.2)	
CO_2	397±154	406±4	392±20	393±16
	(384 – 483)	(398 – 414)	(369 – 540)	(307.0 – 434.0)

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM

Table S6. Average ± StDev (range) of TVOC (μg/m^3) and CO and CO_2 gas (ppm) concentrations by print job during extrusion of PESU polymer.[a]

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
PID				
TVOC	1765±1280	674±540	**	654±380
	(129 – 18804)	(<2.3 – 23339)		(177 – 6324)
Gases				
CO	0.001±0.02	0.5±0.2	2.7±1.0	2.7±0.4
	(0 – 0.7)	(0 – 1.4)	(1.6 – 5.0)	(1.7 – 3.9)
CO_2	726±29	715±30	639±20	629±16
	(640 – 979)	(629 – 850)	(606 – 772)	(585 – 681)

[a] Outside = outside enclosure at operator's station; Inside = inside enclosure at front of LFAM
** = instrument error (no data)

Emission characteristics

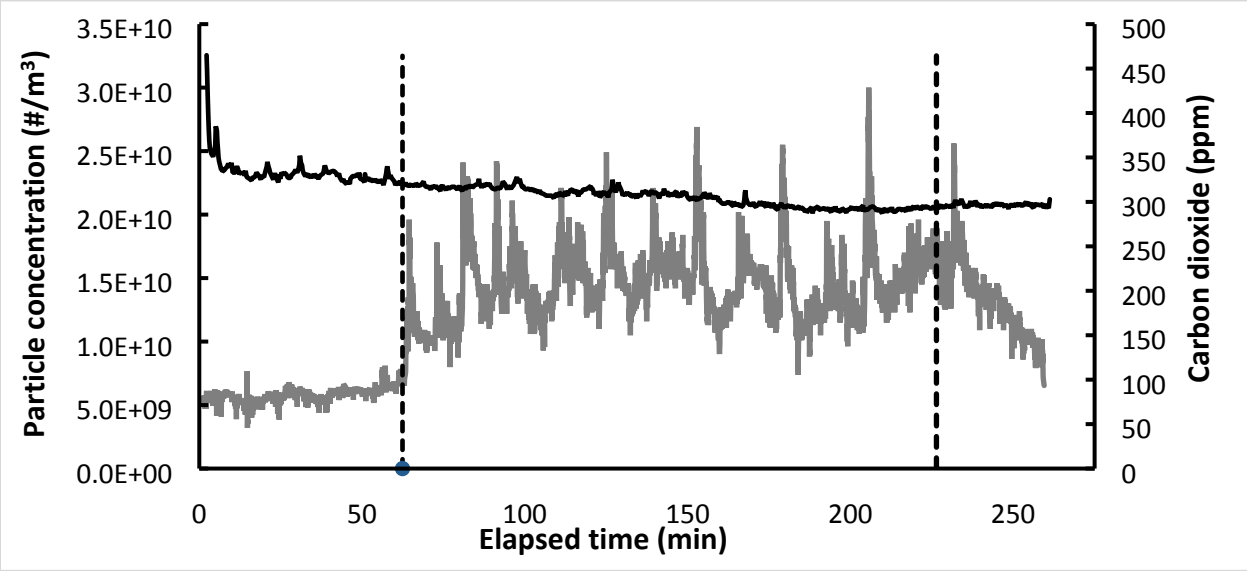

Figure S2. Representative plot of particle number (grey line, primary y-axis) and carbon dioxide (black line, secondary y-axis) concentrations during a PC print illustrating differences in emissions profiles.

Factors influencing emissions

Supplemental Figures S3 – S11 are box plots of particulate emission metrics at the outside and inside sampling locations for the LFAM machine enclosures stratified by nine machine-, feedstock-, and room-related factors that may influence rates and yields. In all plots, the bottom whisker is the 10th percentile, the bottom of the box is the 25th percentile, the line within the box is the median, the top boundary of the box is the 75th percentile; and the top whisker is the 90th percentile. Solid circles are outlier values.

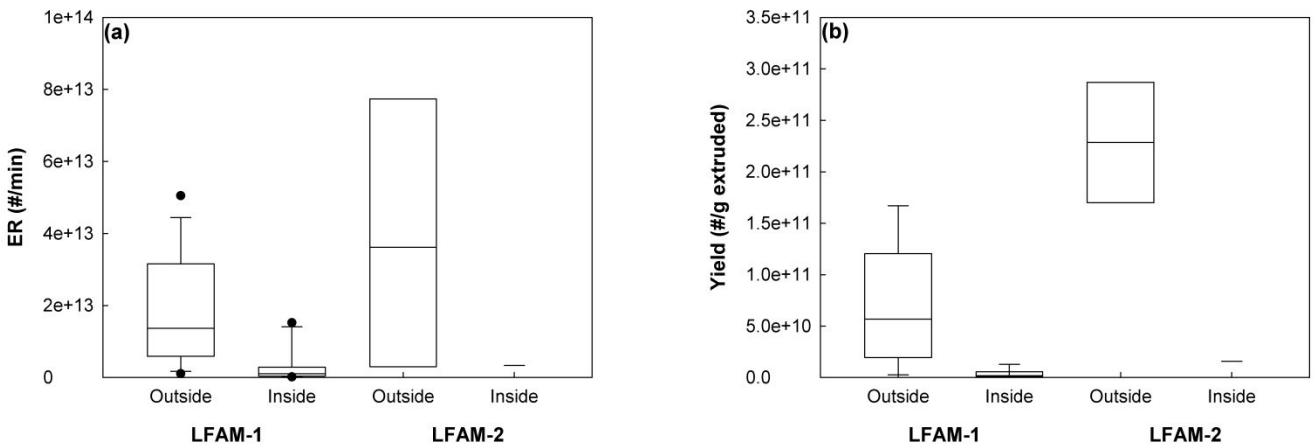

Figure S3. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by LFAM machine. Dash = single data point.

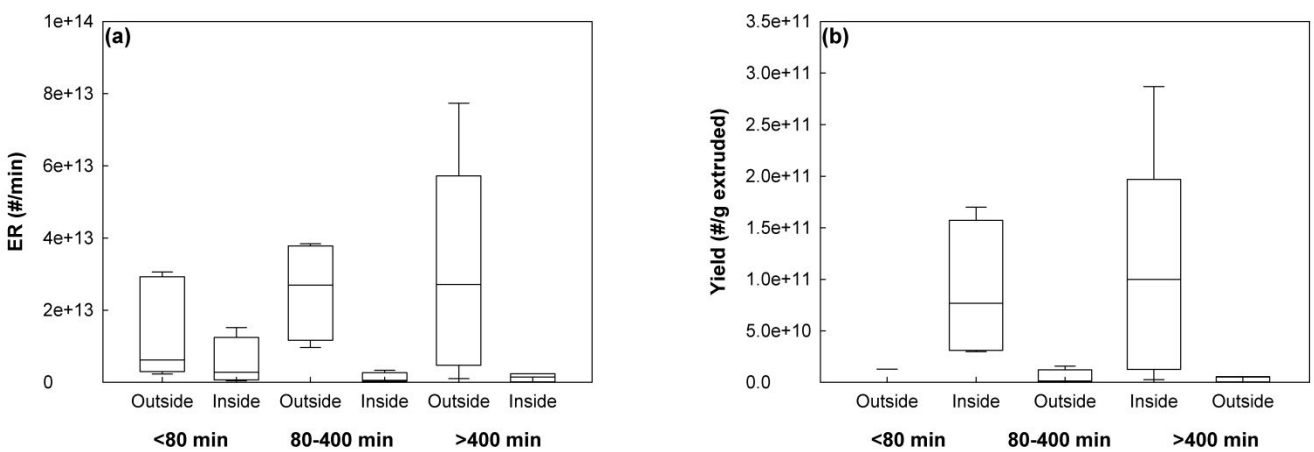

Figure S4. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by tertile of print times. Dash = single data point.

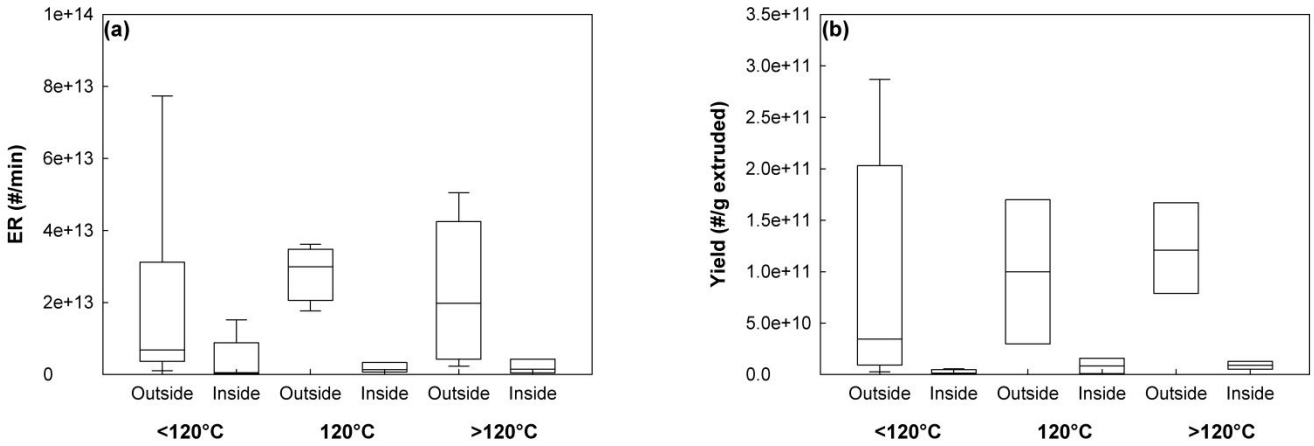

Figure S5. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by tertile of print bed temperatures.

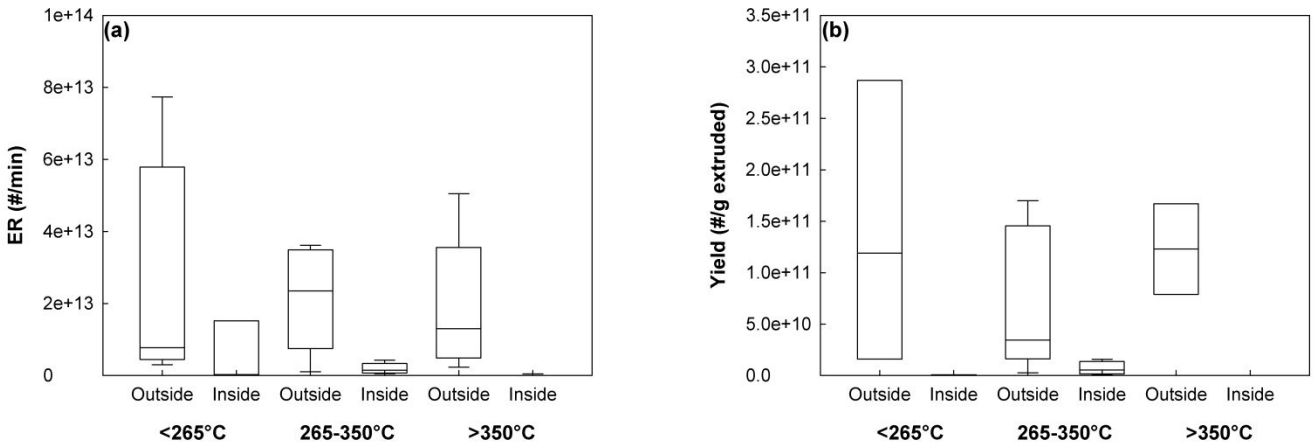

Figure S6. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by tertile of extruder melt temperature. Dash = single data point. Label without box plot indicates no data is available.

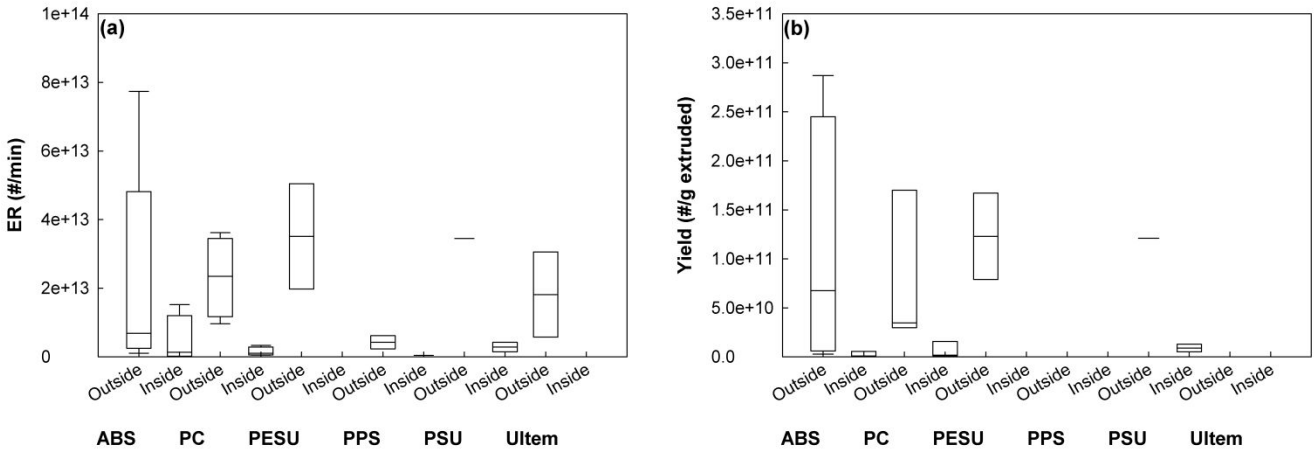

Figure S7. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by polymer type. Dash = single data point. Label without box plot indicates no data is available.

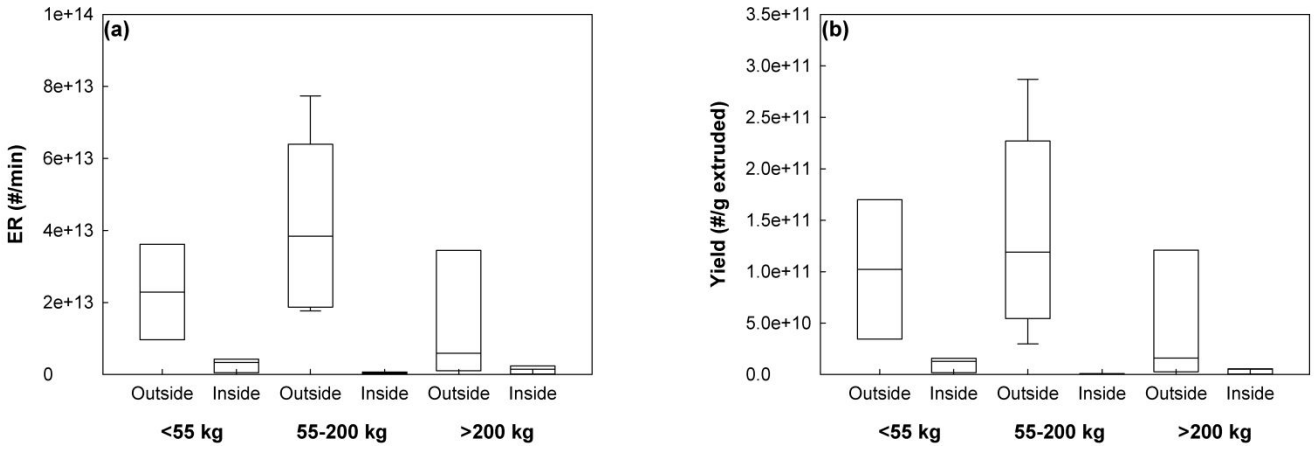

Figure S8. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by tertile of mass of polymer extruded. Dash = single data point.

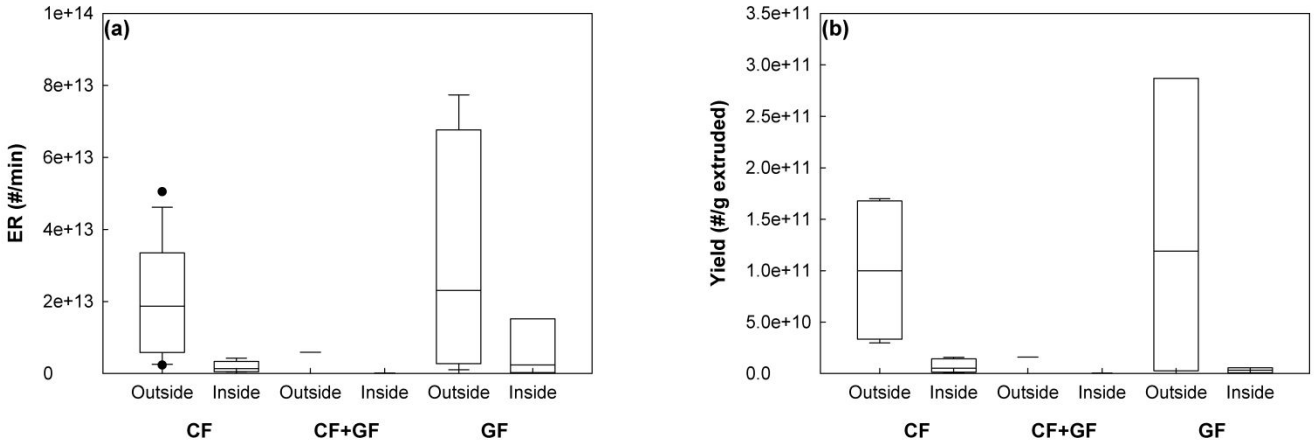

Figure S9. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by polymer infill type. CF = carbon fiber, GF = glass fiber, and CF+GF = mixture of carbon and glass fibers. Dash = single data point. Label without box plot indicates no data is available.

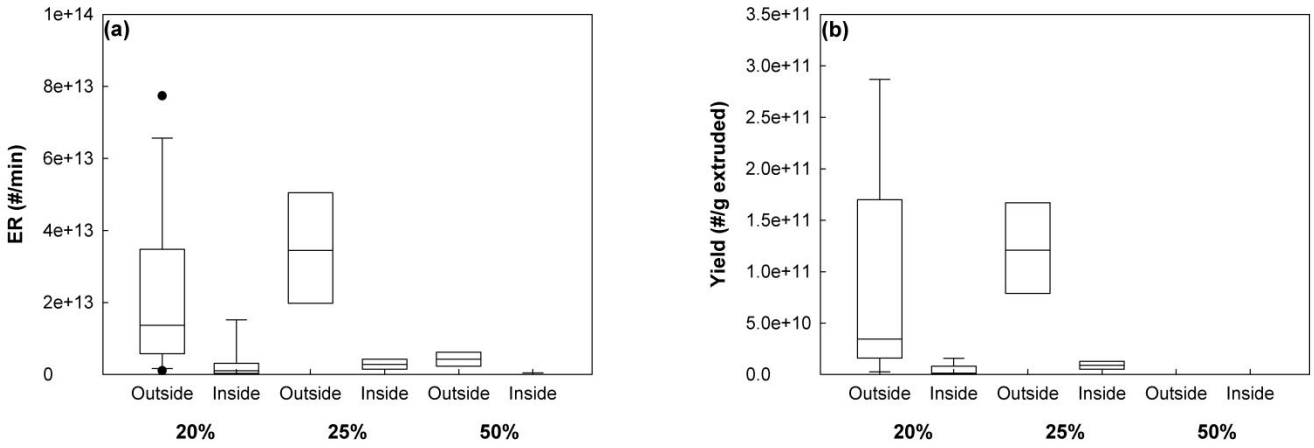

Figure S10. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by polymer infill amount (w/w). Dash = single data point. Label without box plot indicates no data is available.

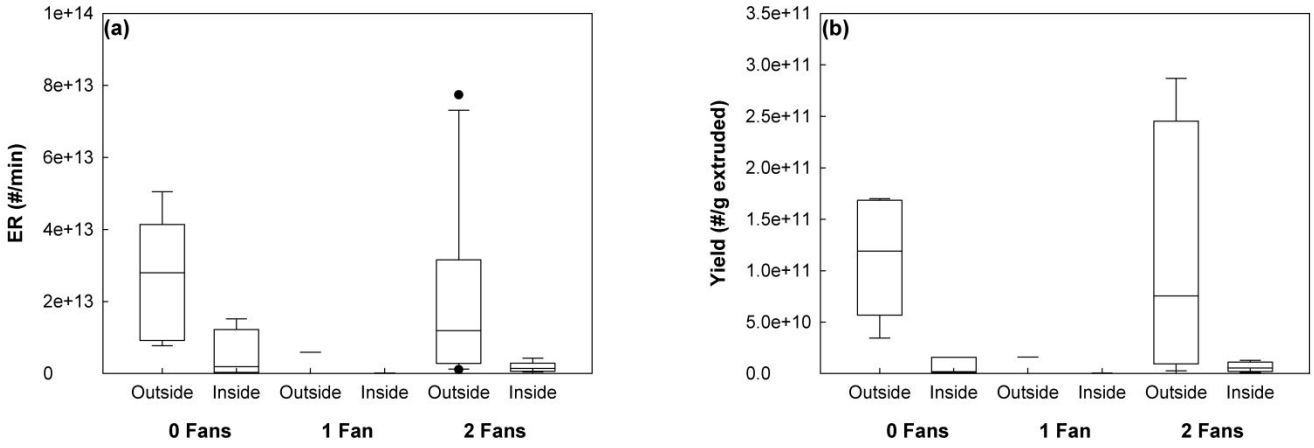

Figure S11. Box plots of particle number emission rate and emission yield for the inside and outside sampling locations by room wall fan usage. Single Dash = single data point. Label without box plot indicates no data is available.

Relationships of CO and CO_2 with particulate and TVOC

As shown in Supplemental Figure S12, average PPS CO concentration was negatively correlated with average TVOC concentration (r_s = -0.63) and average particulate number concentration (r_s = -0.87). Data were insufficient to evaluate correlations for all other combinations of polymer emissions and CO levels. As shown in Supplemental Figure S13, for PC polymer, average CO_2 and average TVOC levels and peak CO_2 and peak TVOC levels were moderately to poorly correlated (r_s = 0.50 and 0.14, respectively). Average and peak PC polymer CO_2 concentrations were moderately correlated with average and peak particle number concentrations (r_s = 0.76 and 0.67, respectively). Peak PPS CO_2 concentration was poorly correlated with peak TVOC concentration (r_s = 0.20) and moderately correlated with peak particle number concentration (r_s = 0.50). Data were insufficient to evaluate correlations for all other combinations of polymer emissions and CO_2 levels.

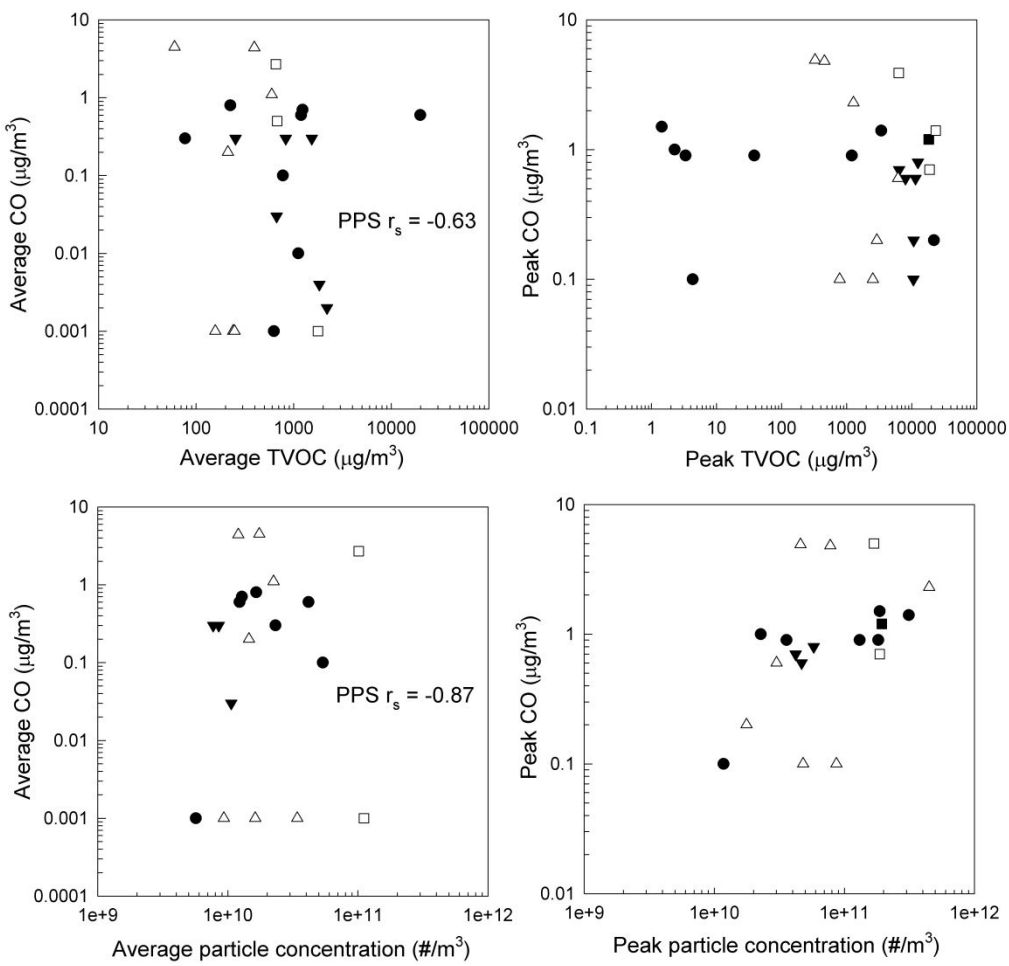

Figure S12. Scatter plots of CO concentrations and LFAM emission metrics. Filled circle = ABS, open circle = Ultem®, inverted filled triangle = PPS, open triangle = PC, filled square = PSU, and open square = PESU.

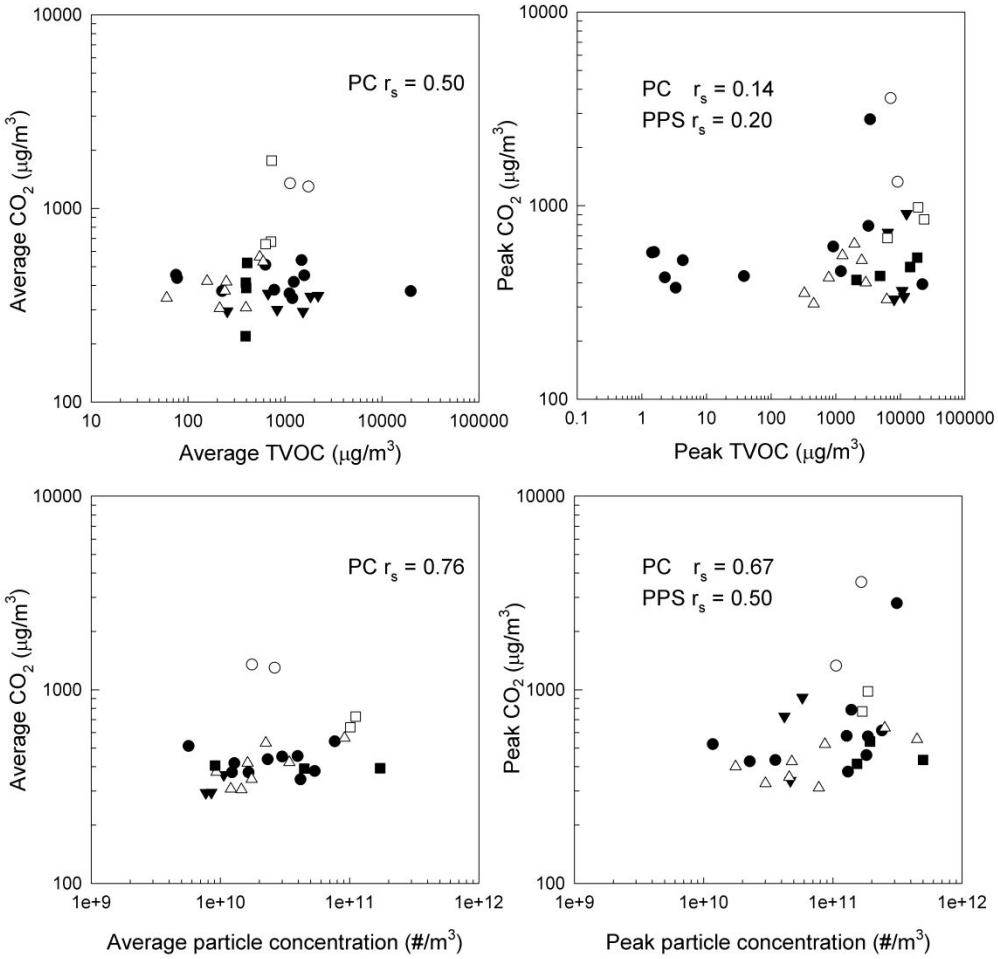

Figure S13. Scatter plots of CO_2 concentrations and LFAM emission metrics. Filled circle = ABS, open circle = Ultem®, inverted filled triangle = PPS, open triangle = PC, filled square = PSU, and open square = PESU.