Supplementary Materials:

Carbonaceous particulate matter emitted from a pellet-fired biomass boiler

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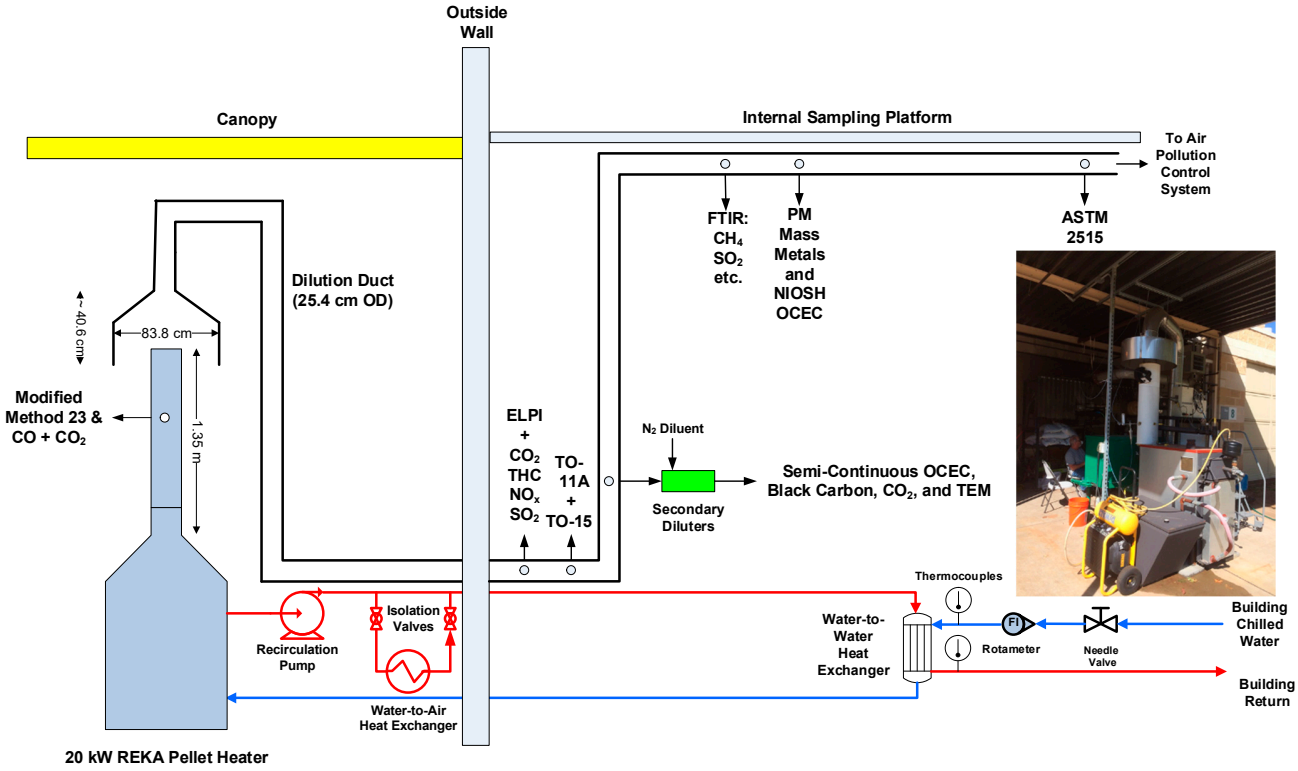
Contents



Schematic 1. Pellet boiler testing facility and BB photo.

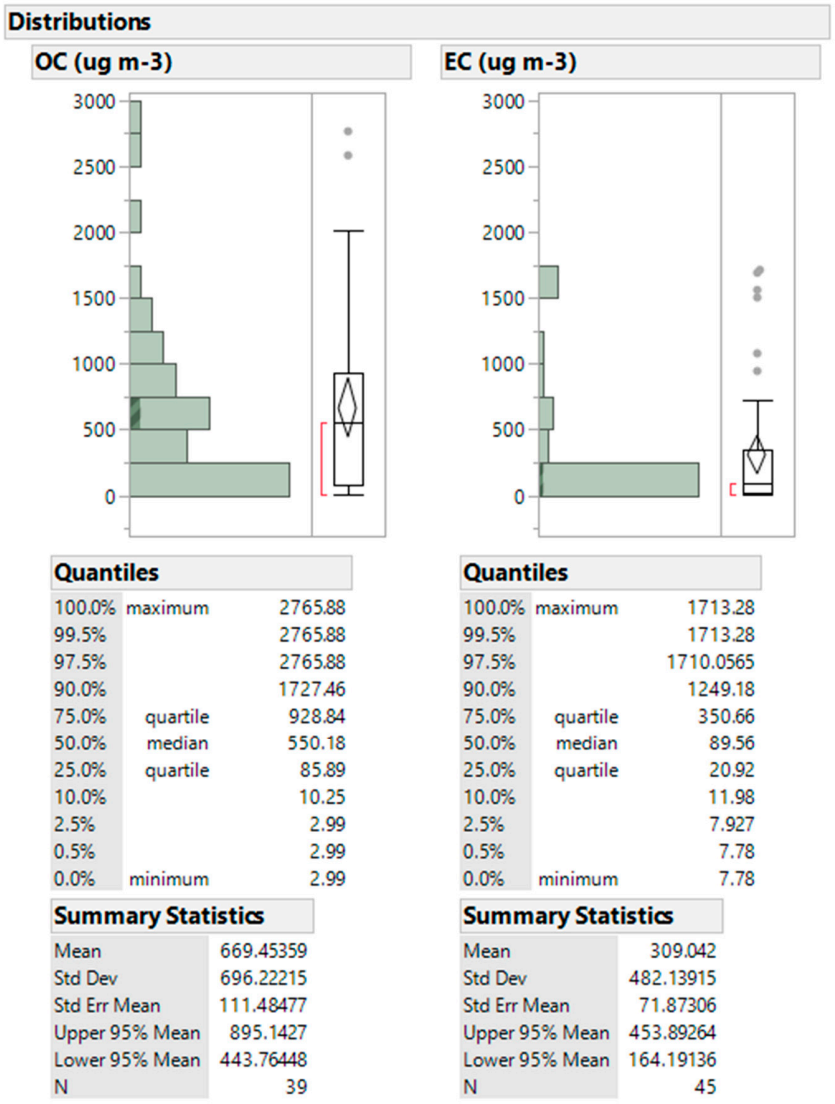


Figure 1. Study-wide distributions, quantiles, and summary statistics for OC-EC concentrations in the PHBB emissions. In the outlier box plot, the confidence diamond contains the mean and the 95% confidence interval about the mean. The red bracket outside the box is referred to as the 'shortest half' or the densest 50% of the observations.

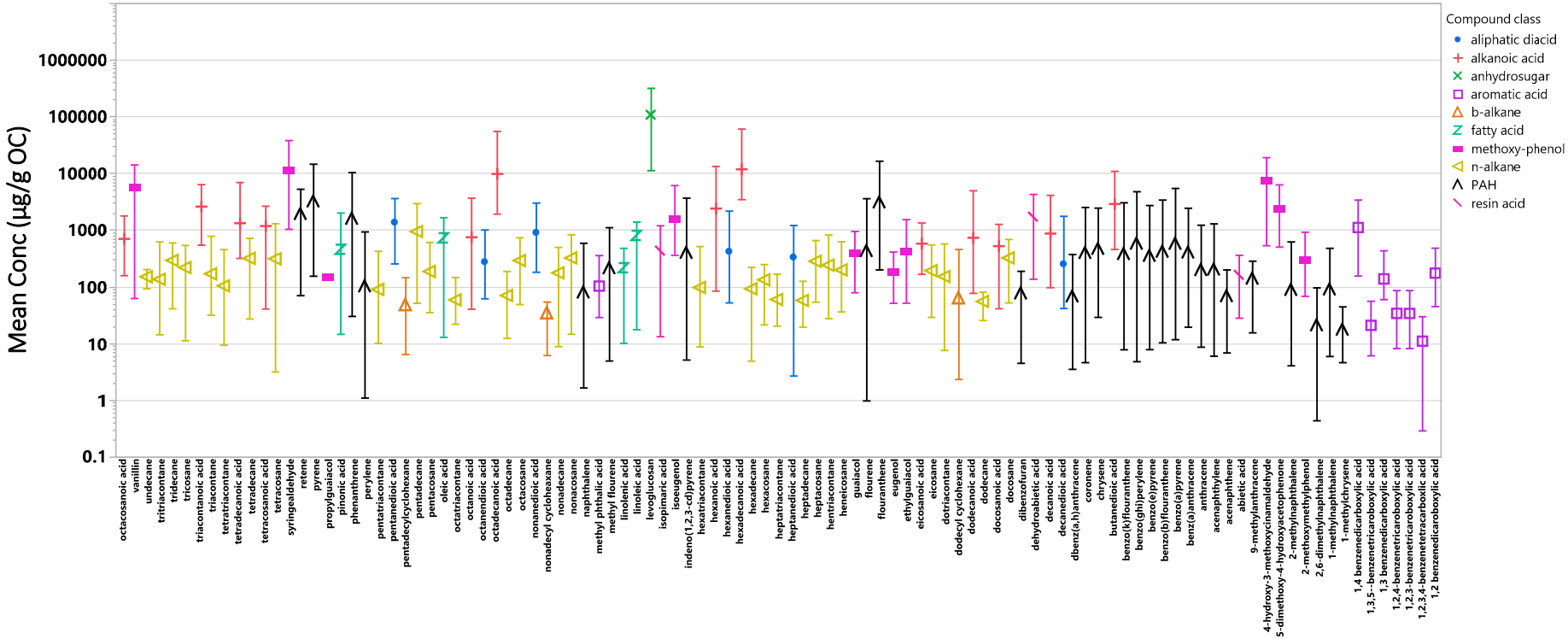


Figure 2. Individual mean SVOC concentrations in PM emitted from boiler testing. Concentrations are given in units of g/g OC. Whiskers indicate the concentration range. The *y*-axis is log scale. Symbols and colors are coded by compound class. The descriptive statistics for each individual compound is provided in Table S2.

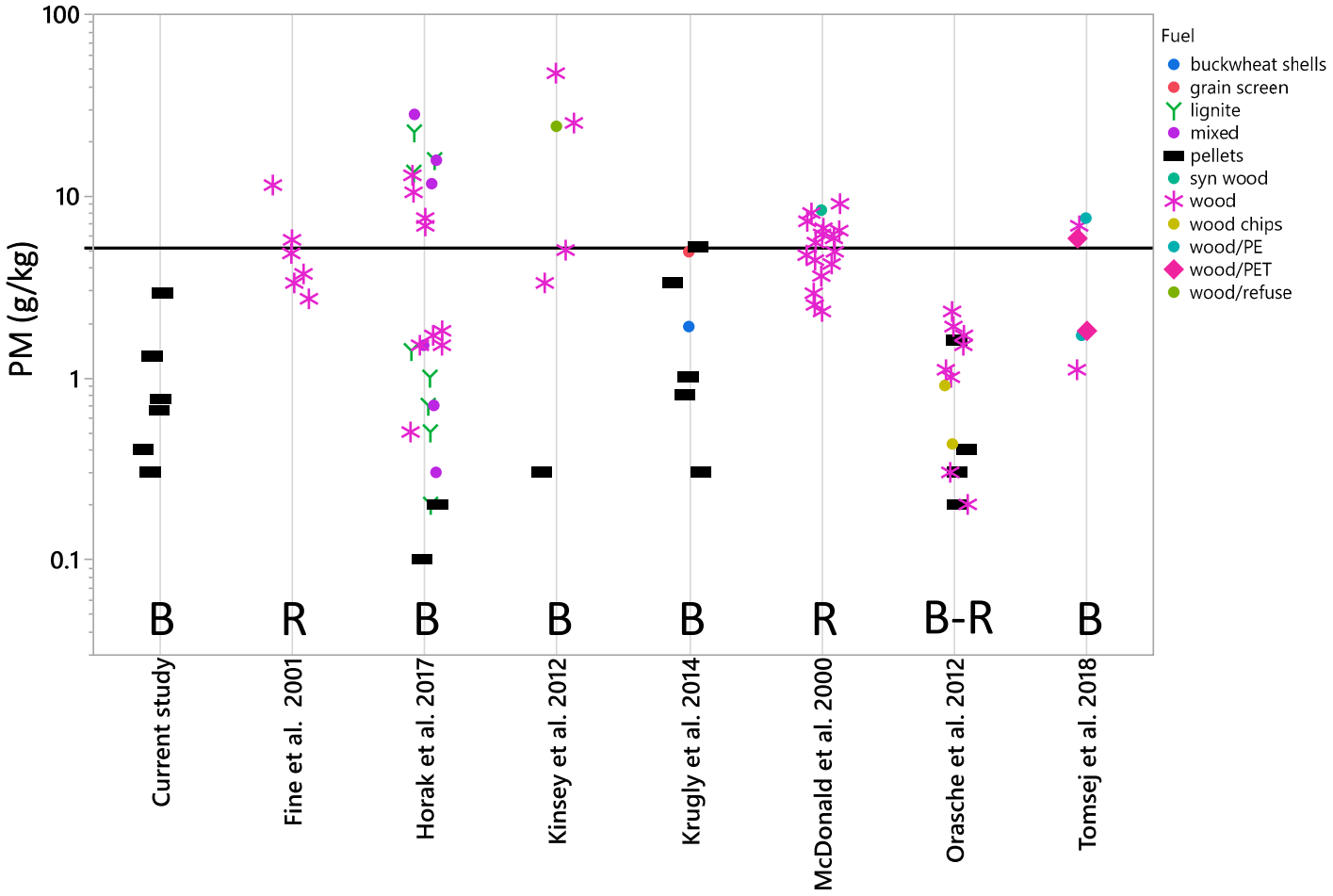


Figure 3. PM emissions factors (g/kg) for a variety of biomass burning studies (n= 87) examining residential (R) fireplace and woodstove and commercial and residential boiler (B) appliances. Fuel type is coded by symbol type and color. Fine et al. 2001[1] and McDonald et al. 2000[2] investigated residential fireplaces and woodstoves. Kinsey et al. 2012[3] tested outdoor wood hydronic heaters (38 kW-50 kW). Tomsej et al. 2018[4] examined a 20 kW commercial boiler. Horak et al. 2017[5] looked at a variety of 20 kW boiler types, including a gasifier, and auto-, over-fire, and down-draft boilers. Krugly et al. 2014[6] looked at a 13 kW boiler, and Orasche et al. 2012[7] studied a boiler and residential stove. The focus is only on studies that report EFs in units of w/w. Horak et al. 2017[5] boiler power is estimated based on nominal power output. Orashe et al. 2012[7] values are converted using their provided fuel calorific value. All values are presented as averages and represent a wide variety of power outputs. The solid line at 5.2 g/kg is the study-wide mean; the median was 2.5 g/kg.

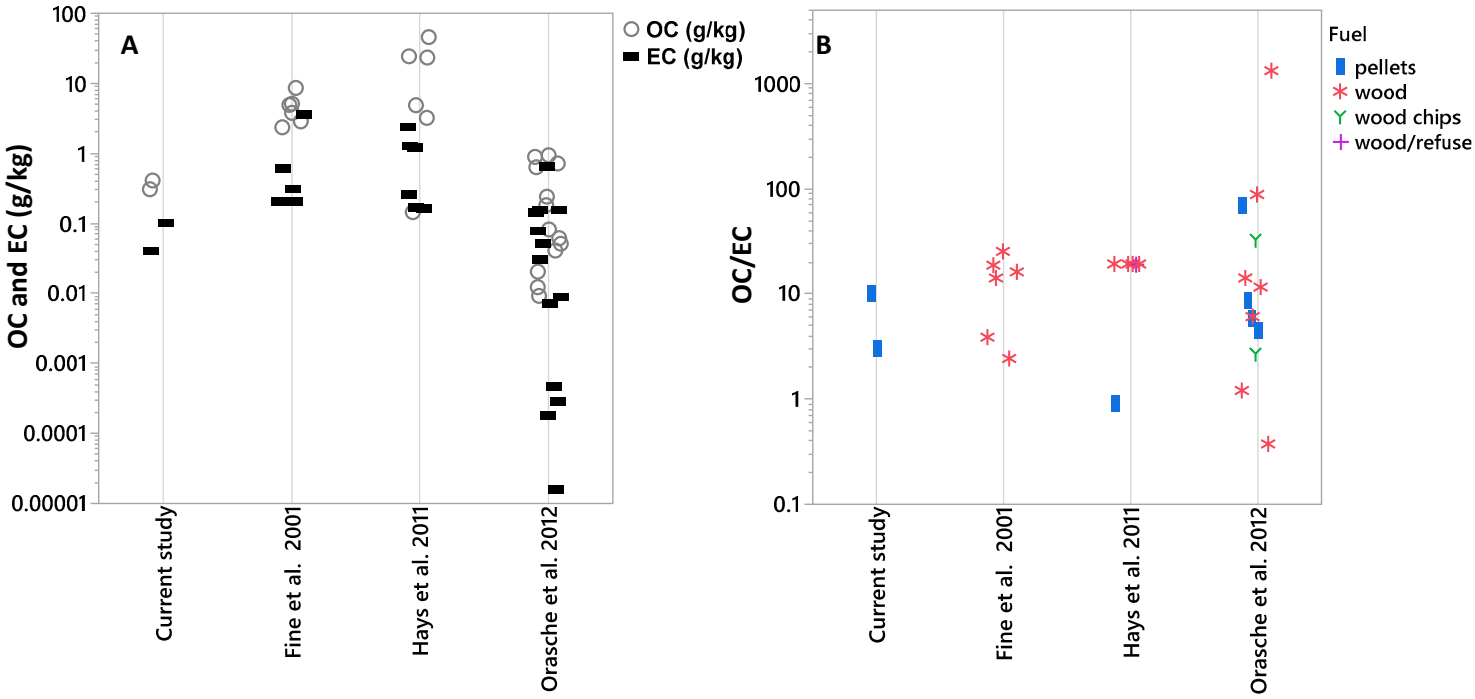


Figure 4. Literature comparison of organic and elemental carbon emission factors (g/kg, Panel A) and OC/EC emissions ratios (Panel B) for PM emitted from biomass burning in residential fireplaces and boiler appliances. Values for the current study are the studies in Figure 3 means by pellet type. In panel B, fuel type is coded by symbol type and color.

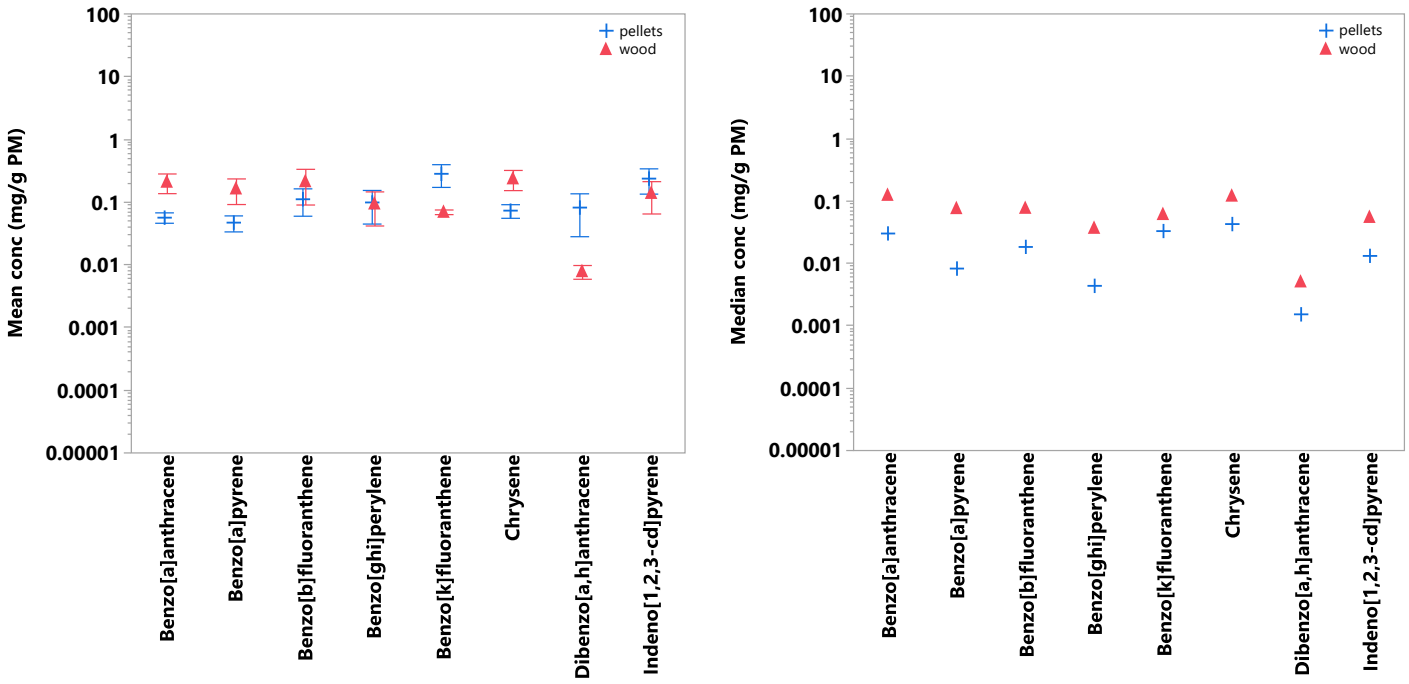


Figure 5. Calculated mean (with standard error) and median values of individual PAH concentrations as determined using the literature values provided in Figure 4. Values are grouped by fuel type.

Table 1. Fuel Analysis Results.

Parameter Measured	Hardwood Pellets	Switchgrass Pellets
Proximate Analysis (as received)		
Moisture	4.66%	10.41%
Volatile Matter	80.34%	72.62%
Fixed Carbon	14.00%	12.71%
Ash	1.00%	4.26%
Ultimate Analysis (as received)		
Sulfur	0.09%	0.12%
Carbon	47.91%	42.79%
Hydrogen	5.79%	5.44%
Nitrogen	0.31%	0.82%
Oxygen (by difference)	40.24%	36.16%
Gross Calorific Value (MJ/kg)	17.99	17.51
Ash Mineral Analysis		
Silicon Dioxide	26.57%	62.99%
Aluminum Oxide	2.40%	7.55%
Ferric Oxide	4.89%	3.63%
Titanium Dioxide	0.27%	0.06%
Phosphorus Pentoxide	0.80%	1.00%
Calcium Oxide	36.63%	10.69%
Magnesium Oxide	2.58%	3.65%
Sodium Oxide	0.44%	1.41%
Potassium Oxide	11.76%	6.42%
Sulfur Trioxide	13.91%	2.32%

Table 2. Descriptive statistics for individual SVOC concentrations in the PM emitted from boiler testing. All experiments are combined. Concentrations are given in units of g/g OC.

Compound	N	Mean	Minimum	Maximum	Median
			Concentration (µg/g OC)		
1,2 benzenedicaroboxylic acid	15	175.27	45.10	485.51	111.03
1,2,3,4-benzenetetracarboxlic acid	4	11.09	0.29	30.03	7.02
1,2,3-benzenetricaroboxylic acid	13	37.76	8.22	86.51	37.58
1,2,4-benzenetricaroboxylic acid	13	37.92	8.22	86.51	38.22
1,3 benzenedicarboxylic acid	13	145.44	60.02	436.48	101.69
1,3,5--benzenetricaroboxylic acid	15	23.14	6.50	56.04	15.48
1,4 benzenedicarboxylic acid	15	1249.44	155.62	3417.97	957.36
1-methylchrysene	14	18.68	4.64	44.63	18.53
1-methylnaphthalene	8	98.49	5.96	480.86	51.27
2,6-dimethylnaphthalene	14	20.62	0.44	96.47	7.86
2-methoxymethylphenol	6	295.80	68.61	929.65	193.52
2-methylnaphthalene	11	94.53	4.08	626.51	24.78
3,5-dimethoxy-4-hydroxyacetophenone	9	2426.72	504.81	6341.00	1687.61
4-hydroxy-3-methoxycinamaldehyde	12	8472.37	536.46	19161.90	7141.53
9-methylanthracene	3	137.56	15.58	286.19	110.92
abietic acid	11	165.33	28.13	362.59	145.11
acenaphthene	4	67.54	6.87	200.32	31.48
acenaphthylene	9	198.74	6.01	1298.41	18.64
anthracene	14	217.84	8.70	1231.92	52.00

benz(a)anthracene	14	415.69	19.55	2450.37	218.71
benzo(a)pyrene	15	628.62	11.79	5478.19	119.49
benzo(b)flouranthene	15	446.47	10.35	3428.09	155.81
benzo(e)pyrene	15	367.59	7.85	2736.06	151.04
benzo(ghi)perylene	15	611.26	4.82	4808.73	171.32
benzo(k)flouranthene	15	406.68	7.81	3059.67	137.92
butanedioic acid	14	3163.55	461.53	10961.41	2316.96
chrysene	15	454.21	29.17	2468.34	251.03
coronene	14	410.16	4.65	2529.31	134.61
dbenz(a,h)anthracene	11	66.80	3.54	375.23	29.31
decanedioic acid	14	273.01	41.76	1766.97	99.18
decanoic acid	13	969.47	97.02	4135.51	450.11
dehydroabietic acid	15	1863.13	136.90	4303.41	1525.64
dibenzofuran	6	75.42	4.51	189.05	50.62
docosane	14	323.74	52.61	690.26	289.11
docosanoic acid	13	509.91	41.43	1273.86	417.62
dodecane	3	54.54	25.66	81.19	56.76
dodecanoic acid	13	827.99	77.59	4988.45	267.92
dodecyl cyclohexane	15	65.36	2.34	461.21	12.07
dotriacontane	13	150.22	7.61	575.14	87.70
eicosane	14	186.74	29.15	554.46	174.58
eicosanoic acid	14	631.12	167.77	1343.29	411.58
ethylguaiacol	6	420.25	51.98	1543.88	243.72
eugenol	4	186.40	51.55	415.02	139.51
flouranthene	15	3086.69	200.58	16589.76	1409.59
flourene	11	421.14	0.98	3618.80	13.05
guaiacol	7	302.15	78.99	796.84	257.73
heneicosane	15	195.57	36.34	627.50	189.68
hentriacontane	14	237.92	27.76	823.83	120.24
heptacosane	10	278.93	54.06	660.25	266.45
heptadecane	12	56.85	19.65	126.56	39.85
heptanedioic acid	10	379.41	2.69	1219.78	135.31
heptatriacontane	5	59.14	20.39	168.23	34.78
hexacosane	10	131.19	21.43	248.70	123.07
hexadecane	14	81.63	4.92	222.79	45.38
hexadecanoic acid	14	13078.73	3472.38	61161.77	6601.71
hexanedioic acid	14	455.68	52.65	2186.71	201.60
hexanoic acid	10	2827.19	84.59	13415.56	995.74
hexatriacontane	9	96.29	8.77	518.91	31.33
indeno(1,2,3-cd)pyrene	15	436.90	5.17	3699.12	77.20
isoeugenol	10	1812.38	363.57	6155.78	1268.15
isopimaric acid	12	489.70	13.30	1204.98	367.35
levoglucosan	15	119856.68	12505.33	320299.65	95405.10
linoleic acid	11	744.41	17.66	1402.49	775.72
linolenic acid	13	225.81	10.14	481.95	170.81
methyl flourene	10	209.85	4.95	1111.99	44.68
methyl phthalic acid	15	113.01	29.05	357.80	75.31
naphthalene	10	85.01	1.66	591.93	31.20
nonacosane	13	319.67	14.71	835.73	163.26
nonadecane	13	174.44	8.86	500.37	151.11
nonadecyl cycloheaxane	6	34.22	6.20	54.26	32.81
nonanedioic acid	14	963.59	182.33	3026.44	785.32

octacosane	7	288.01	49.09	736.70	279.44
octadecane	12	65.30	12.42	188.27	55.52
octadecanoic acid	14	10926.94	1928.61	55466.81	5184.66
octanendioic acid	14	299.63	62.04	1011.32	216.07
octanoic acid	16	753.49	40.75	3692.13	486.49
octatriacontane	4	58.08	22.03	147.39	31.45
oleic acid	14	731.91	12.96	1672.13	559.79
pentacosane	14	191.54	35.42	610.34	167.82
pentadecane	9	929.93	51.55	2962.45	420.38
pentadecylcyclohexane	9	47.80	6.43	145.82	29.72
pentanedioic acid	15	1403.60	255.56	3638.27	1228.62
pentatriacontane	11	88.78	10.14	425.34	31.48
perylene	14	112.74	1.10	937.08	24.56
phenanthrene	15	1722.41	30.29	10425.53	414.08
pinonic acid	10	531.87	14.64	2019.62	93.26
propylguaiacol	2	149.56	146.59	152.53	149.56
pyrene	15	3024.19	154.97	14632.47	1056.82
retene	15	1984.62	70.40	5311.90	1314.23
syringealdehyde	15	12500.04	1043.16	38283.93	8658.35
tetracosane	15	299.73	3.17	1305.56	231.03
tetracosanoic acid	14	983.38	40.87	2636.94	859.56
tetradecane	5	385.06	27.20	724.17	518.83
tetradecanoic acid	14	1468.22	319.37	6961.07	706.18
tetratriacontane	11	103.08	9.44	456.80	29.83
triacontane	14	182.65	31.79	785.26	97.33
triacontanoic acid	6	2626.12	547.13	6394.53	2146.70
tricosane	15	216.74	11.31	542.27	210.92
tridecane	5	326.82	41.29	598.93	319.62
tritriacontane	13	134.35	14.42	624.64	56.42
undecane	2	148.50	92.86	204.14	148.50
vanillin	13	5047.37	62.59	14267.25	5188.31
octacosanoic acid	5	923.57	307.81	1793.44	923.51

Emission factor calculations

For each test run, emission factors for the target pollutants were calculated in terms of mass of fuel burned. The mass emission (M_x) for a set burn time t for each target compound is calculated in the dilution tunnel as follows:

$$M_x = \sum_t (C_{x,t} - C_{x,a}) \cdot V \cdot t \quad (1)$$

Where:

$C_{x,t}$ = the concentration (mass/volume) of the target compound x in the dilution duct,

$C_{x,a}$ = the ambient concentration (mass/volume) of the target compound x, and

V = the volumetric flow rate (volume/time) in the dilution tunnel at time t.

Most concentrations were determined on a test average basis. The ambient concentration for total PM utilized an ambient air sample extracted beside the boiler during 100% load operation firing switchgrass pellets. Remaining concentrations were corrected with concentrations determined from dilution duct sampling with no firing (i.e. cold) of the boiler.

Volumetric flow rate was determined by multiplying the average of the dilution duct velocity measured before and after each test by the cross-sectional area of the dilution duct at the point measured. The 10-inch duct had a cross-sectional area of 0.0506 m² (0.545 ft²).

Emission factors were calculated and reported per mass of fuel burned.

The emission factor per mass of fuel burned ($EF_{m,x}$) is calculated as:

$$EF_{m,x} = \frac{M_x}{M_f} \quad (2)$$

Dilution Factor

Measurements made at the stack or after secondary dilution were corrected to dilution duct concentrations using a dilution factor. Due to failure in the CEM measurements, estimates were made for CO_2 concentrations in the dilution duct for use in dilution factor calculations. The average CO_2 in the dilution duct was estimated based on the mass of fuel burned in each test (M_f), the carbon concentration in the fuel from the ultimate analysis, and the volumetric flow rate determined for the test. The calculation estimates the volume of CO_2 emitted divided by the volume of flow in the dilution duct corrected for ambient CO_2 concentration:

$$C_{CO2,t} = \frac{M_f \cdot \%C}{100 \cdot t} \cdot \frac{1}{MW_{Carbon}} \cdot \frac{SV}{V} + C_{CO2,a} \quad (3)$$

Where:

$C_{CO2,t}$ = the CO_2 concentration in the duct,

$C_{CO2,a}$ = the ambient concentration of CO_2,

$\%C$ = the carbon concentration in the fuel (weight percent),

MW_{Carbon} = the molecular weight of carbon, and

SV = the specific volume of an ideal gas at 20 °C and 1 atmosphere.

Concentrations measured at the stack or on secondary dilution were corrected to dilution duct concentrations for emission calculations.

The dilution factor at the stack were based on the estimated dilution duct CO_2 concentration and the average stack CO_2 concentration:

$$DF = \frac{C_{CO2,t} - C_{CO2,a}}{Stack\ CO2} \quad (4)$$

The dilution used for secondary dilution was performed with nitrogen containing minimal CO_2:

$$DF = \frac{C_{CO2,t}}{SD_{CO2,t}} \quad (5)$$

Where:

$SD_{CO2,t}$ = Secondary dilution CO_2 concentration during sample interval

Because the nature of operations and the short-term nature of the measurements taken on secondary dilution, each measurement was corrected using time specific dilution factors. Due to the quality of duct CO_2 measurement, time specific dilution duct CO_2 concentrations were estimated using the average dilution duct CO_2 measurements for the specific sampling time, average dilution duct CO_2 concentrations for total test, and the average fuel based estimate of dilution duct CO_2 concentrations calculated as above:

$$C_{CO2,t} = \frac{Fuel\ Based\ Average\ CO2}{CEM\ Test\ average\ CO2} \cdot CEM\ sample\ average\ CO2 \quad (6)$$

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