Table S1

The fraction of the compounds (%) detected in samples of one quantification batch (sample No. = 79) falling within, below and above the calibration range.

Molecular markers	Within	Below	Above	Molecular markers	Within	Below	Above
n-Alkanes				*Steranes*			
docosane	62.0	1.27	36.7	20R-abb & 20S-aaa-cholestane	84.8	3.80	11.4
tricosane	64.6	1.27	34.2	20R & S-abb-methylcholestane	79.8	13.9	6.33
tetracosane	86.1	1.27	12.7	20R & S-abb-ethylcholestane	86.1	2.53	11.4
pentacosane	81.0	1.27	17.7	a-22,29,30-trisnorhopane	81.0	2.53	16.5
hexacosane	88.6	10.1	1.27	ba-30-norhopane	35.4	1.27	63.3
heptacosane	83.5	10.1	6.33	ab-hopane	58.2	1.27	40.5
octacosane	84.8	15.2	0.00	22S-ab-30-homohopane	79.8	5.06	15.2
nonacosane	76.0	5.06	19.0	22R-ab-30-homohopane	83.5	6.33	10.1
triacontane	68.4	31.7	0.00	22S-ab-30-bishomohopane	81.0	13.9	5.06
hentriacontane	76.0	6.33	17.7	22R-ab-30-bishomohopane	83.5	13.9	2.53
dotriacontane	62.0	38.0	0.00				
tritriacontane	86.1	13.9	0.00	*n-Alkanoic acids*			
tetratriacontane	69.6	30.4	0.00	dodecanoic acid	39.2	0.00	60.8
pentatriacontane	54.4	45.6	0.00	tridecanoic acid	70.9	20.3	8.86
				tetradecanoic acid	30.4	0.00	69.6
PAHs				pentadecanoic acid	92.4	1.27	6.33
fluoranthene	53.2	0.00	46.8	hexadecanoic acid	1.27	0.00	98.7
pyrene	55.7	1.27	43.0	heptadecanoic acid	60.8	39.2	0.00
benzo[ghi]fluoranthene	68.4	2.53	29.1	octadecanoic acid	10.1	0.00	89.9
cyclopenta[cd]pyrene	58.2	39.2	2.53				
benz[a]anthracene	63.3	27.9	8.86	*Sterols and methoxyphenols*			
chrysene/triphenylene	50.6	1.27	48.1	cholesterol	91.1	3.80	5.06
benzo[b&k]fluoranthene	84.8	10.1	5.06	stigmasterol	69.6	25.3	5.06
benz[a&e]pyrene	82.3	12.7	5.06	acetovanillone	41.8	58.2	0.00
indeno[1,2,3-cd]pyrene	82.3	8.86	8.86	vanillin	69.6	1.27	29.1
benzo[ghi]perylene	84.8	3.80	11.4	syringealdehyde	58.2	10.1	31.7
coronene	91.1	3.80	5.06	coniferaldehyde	65.8	32.9	1.27
2-methylfluoranthene	70.9	1.27	27.9	acetosyringone	15.2	84.8	0.00
methyl-202-PAH sum	34.2	1.27	64.6				
retene	67.1	5.06	27.9				
fluorenone	39.2	0.00	60.8				
1H-phenalen-1-one	50.6	1.27	48.1				
xanthone	68.4	1.27	30.4				
1,8-naphthalic anhydride	53.2	1.27	45.6				
anthracene-9,10-dione	27.9	1.27	70.9				
benz[de]anthracene-7-one	78.5	15.2	6.33				

Table S2

Statistics for $PM_{2.5}$ carbonaceous components at the four sampling sites (March 1, 2008-March 14, 2009).

Molecular Marker	Abbr.	PAL (*N*=63)					EDI (*N*=59)					ALS (*N*=63)					MAS (*N*=62)				
(ng m^{-3})		Mean	Median	CV[a]	S/N[b]	BDL (%)[c]	Mean	Median	CV	S/N	BDL (%)	Mean	Median	CV	S/N	BDL (%)	Mean	Median	CV	S/N	BDL (%)
n-Alkanes																					
docosane	C22	2.19	1.62	0.94	8.56	2	2.00	1.50	1.15	8.33	0	2.23	1.85	0.88	8.50	0	1.66	1.47	0.71	8.54	0
tricosane	C23	4.00	1.98	1.33	11.2	0	3.10	1.77	1.05	10.7	0	2.75	1.78	0.94	10.4	0	2.30	1.58	0.88	10.7	0
tetracosane	C24	1.89	1.17	1.04	13.1	0	1.11	0.83	0.92	12.2	0	1.25	1.00	0.83	12.6	0	1.05	0.76	0.75	12.5	0
pentacosane	C25	1.88	1.13	1.03	10.8	0	1.66	0.98	1.05	10.8	0	1.69	1.17	0.89	10.8	0	1.62	1.11	0.85	11.2	0
hexacosane	C26	0.85	0.59	1.01	9.43	2	0.56	0.43	0.76	6.73	2	0.73	0.52	1.00	8.51	0	0.66	0.50	0.87	8.98	0
heptacosane	C27	1.64	0.87	1.25	12.7	0	1.31	0.68	0.94	11.2	0	1.62	0.93	1.22	12.3	0	1.42	0.83	1.02	12.8	0
octacosane	C28	0.82	0.48	1.12	9.24	6	0.62	0.37	1.04	7.08	5	0.89	0.44	1.87	9.35	3	0.73	0.38	1.26	9.25	5
nonacosane	C29	4.20	1.60	1.89	13.8	0	3.43	1.54	1.52	13.4	0	4.36	1.49	2.26	13.1	0	3.51	1.56	1.57	13.7	0
triacontane	C30	0.92	0.47	1.36	9.96	5	0.67	0.39	1.26	7.24	12	0.74	0.35	1.26	8.03	13	0.82	0.41	1.26	10.2	5
hentriacontane	C31	11.2	2.39	2.04	11.9	0	9.66	2.50	1.74	11.9	0	12.4	2.54	2.57	11.4	0	9.67	3.93	1.64	11.9	0
dotriacontane	C32	0.20	0.14	1.00	4.37	17	0.15	0.12	1.12	3.60	15	0.16	0.12	1.28	3.75	17	0.17	0.12	1.27	4.21	11
tritriacontane	C33	0.36	0.22	1.22	7.14	0	0.32	0.18	1.22	6.32	0	0.32	0.20	1.31	6.73	0	0.35	0.21	1.31	7.57	0
tetratriacontane	C34	0.22	0.13	1.24	7.32	8	0.18	0.10	1.18	6.18	3	0.21	0.14	1.23	6.91	8	0.20	0.11	1.23	7.08	5
pentatriacontane	C35	0.16	0.09	1.27	7.47	16	0.09	0.07	1.25	4.75	24	0.12	0.08	1.04	5.51	22	0.11	0.08	0.95	5.93	16
Subtotal		30.5	12.7	1.41			24.9	12.9	1.17			29.4	12.0	1.66			24.3	15.3	1.16		
PAHs																					
fluoranthene	Flu	0.21	0.16	0.86	13.1	0	0.24	0.17	1.00	14.0	0	0.40	0.30	0.81	15.3	0	0.35	0.31	0.68	15.6	0
pyrene	Pyr	0.13	0.11	1.31	12.5	0	0.17	0.08	1.50	13.9	0	0.29	0.20	0.94	14.0	0	0.23	0.20	0.71	13.6	0
benzo[ghi]fluoranthene	BghiF	0.08	0.06	1.03	19.3	0	0.11	0.08	1.19	23.6	0	0.17	0.12	0.97	22.9	0	0.16	0.14	0.80	24.2	0
cyclopenta[cd]pyrene	C-pyr	0.04	0.02	1.30	10.1	5	0.04	0.02	1.31	9.99	12	0.05	0.04	1.09	11.4	3	0.06	0.03	1.39	13.3	3
benz[a]anthracene	BaA	0.05	0.02	1.50	12.1	8	0.07	0.04	1.34	15.3	3	0.09	0.06	1.13	15.4	0	0.11	0.06	1.57	17.4	2
chrysene/triphenylene	CT	0.18	0.13	1.03	16.7	0	0.23	0.19	0.99	17.6	0	0.33	0.24	0.89	17.1	0	0.33	0.21	0.87	18.0	0
benzo[b&k]fluoranthene	BbkF	0.22	0.10	1.21	14.5	0	0.28	0.17	1.15	15.6	0	0.36	0.17	1.12	15.5	0	0.37	0.24	1.13	17.0	0
benz[a&e]pyrene	BaeP	0.18	0.09	1.15	10.6	3	0.21	0.15	1.13	11.3	0	0.28	0.15	1.12	12.8	0	0.29	0.19	1.11	14.6	0
indeno[1,2,3-cd]pyrene	IP	0.03	0.02	0.98	8.26	6	0.03	0.02	0.79	7.86	7	0.04	0.02	0.99	9.84	6	0.05	0.03	0.97	12.1	5
benzo[ghi]perylene	BP	0.06	0.04	0.89	8.16	3	0.06	0.05	0.72	7.57	3	0.09	0.06	0.91	9.81	3	0.09	0.08	0.71	11.3	0
coronene	Cor	0.03	0.02	0.82	9.58	2	0.03	0.02	0.76	9.55	2	0.04	0.03	0.92	11.0	0	0.04	0.03	0.80	11.1	0
2-methylfluoranthene	2M-Flu	0.20	0.14	1.01	14.5	2	0.22	0.13	1.21	14.6	0	0.29	0.24	0.79	15.8	0	0.25	0.22	0.67	16.3	0
methyl-202-PAH sum	M-202	0.68	0.47	1.24	16.9	0	0.72	0.52	1.06	16.8	0	1.05	0.84	0.86	17.1	0	0.83	0.77	0.71	17.5	0
retene	Ret	0.72	0.28	1.69	16.3	6	0.64	0.24	1.50	15.4	5	0.41	0.20	1.16	13.2	8	0.43	0.20	1.37	14.7	5
Sub total		2.60	1.94	1.05			2.85	2.24	1.01			3.60	3.10	0.78			3.34	2.84	0.74		
Oxy-PAHs																					
fluorenone	Flu-O	1.08	0.57	1.14	17.0	0	1.36	0.79	1.12	17.8	0	1.24	0.74	1.13	16.7	0	1.22	0.56	1.31	18.4	0
1H-phenalen-1-one	Phe-O	0.45	0.26	1.19	18.4	0	0.66	0.50	0.97	18.8	2	0.93	0.58	0.98	17.9	0	0.65	0.38	1.32	18.8	0
xanthone	Xan	0.25	0.11	1.26	16.8	0	0.27	0.13	1.22	17.4	2	0.26	0.13	1.15	15.8	0	0.21	0.12	1.09	16.5	2
1,8-naphthalic anhydride	Nap-DO	0.38	0.16	1.39	18.4	0	0.52	0.21	1.50	19.3	0	0.60	0.27	1.57	17.8	0	0.46	0.21	1.32	18.8	0
anthracene-9,10-dione	Ant-DO	0.53	0.23	1.26	18.9	0	0.57	0.35	0.98	19.2	0	0.78	0.43	1.16	17.8	0	0.67	0.34	1.19	18.7	0
benz[de]anthracene-7-one	BaA-O	0.06	0.04	1.12	14.9	2	0.08	0.05	1.11	16.7	0	0.10	0.06	1.00	16.1	0	0.10	0.06	1.11	17.2	0
Subtotal		2.75	2.34	0.71			3.47	3.56	0.61			3.92	3.28	0.71			3.32	2.71	0.70		

[a] Coefficient of variation (CV) = standard deviation/mean concentration; [b] Signal to noise ratio (mean concentration/mean uncertainty); [c] Percent of observations not significantly different from zero using a p-value of 0.05.

Table S2 (*continued*)

Molecular Marker	Abbr.	PAL (*N*=63)					EDI (*N*=59)					ALS (*N*=63)					MAS (*N*=62)				
(ng m^{-3})		Mean	Median	CV	S/N	BDL (%)	Mean	Median	CV	S/N	BDL (%)	Mean	Median	CV	S/N	BDL (%)	Mean	Median	CV	S/N	BDL (%)
Steranes																					
20R-abb & 20S-aaa-cholestane	27-RS-C	0.19	0.11	1.03	21.5	0	0.21	0.14	0.91	22.2	0	0.23	0.18	0.82	20.5	0	0.27	0.17	0.96	23.8	2
20R & S-abb-methylcholestane	28-RS-M	0.10	0.04	1.32	19.8	16	0.10	0.06	1.11	19.2	5	0.15	0.08	1.13	15.8	5	0.14	0.09	1.05	18.7	2
20R & S-abb-ethylcholestane	29-RS-E	0.11	0.09	0.79	16.3	2	0.11	0.09	0.85	16.5	2	0.16	0.11	1.05	16.2	0	0.13	0.10	0.78	17.0	2
a-22,29,30-trisnorhopane	TS	0.14	0.08	1.04	17.2	3	0.15	0.10	1.03	17.8	0	0.16	0.11	0.94	17.6	0	0.16	0.12	0.88	19.2	0
ba-30-norhopane	ba-N	0.25	0.21	0.74	18.2	0	0.28	0.24	0.73	18.6	0	0.42	0.31	0.91	16.9	0	0.38	0.32	0.68	18.2	0
ab-hopane	ab-H	0.19	0.13	0.90	14.4	0	0.21	0.15	0.91	14.4	2	0.31	0.18	1.00	14.3	0	0.28	0.21	0.80	14.9	0
22S-ab-30-homohopane	31abS	0.15	0.09	1.18	13.4	3	0.14	0.10	1.35	13.4	7	0.19	0.12	1.23	13.3	5	0.17	0.11	1.01	14.4	2
22R-ab-30-homohopane	31abR	0.13	0.08	1.24	12.9	6	0.12	0.08	1.25	12.8	12	0.16	0.12	1.18	13.0	5	0.14	0.09	0.92	13.9	3
22S-ab-30-bishomohopane	32abS	0.09	0.05	1.43	10.8	22	0.11	0.09	1.16	12.0	12	0.14	0.09	1.05	12.6	11	0.11	0.08	1.14	13.5	10
22R-ab-30-bishomohopane	32abR	0.08	0.04	1.37	10.6	24	0.10	0.08	1.20	11.5	15	0.12	0.08	1.20	12.3	13	0.11	0.07	1.30	13.3	10
subtotal		1.43	1.01	0.90			1.52	1.19	0.86			2.03	1.66	0.86			1.89	1.37	0.79		
n-alkanoic acids																					
dodecanoic acid	C12:0	30.9	6.62	1.39	10.5	2	30.3	6.95	1.33	10.4	3	31.9	6.36	1.39	10.2	2	24.3	5.65	1.45	10.5	2
tridecanoic acid	C13:0	2.98	0.71	1.47	8.05	13	3.35	0.86	1.46	8.05	14	3.82	0.61	1.52	8.06	24	3.35	0.75	1.55	8.19	13
tetradecanoic acid	C14:0	18.0	4.19	1.40	9.54	2	23.8	6.12	1.43	9.51	0	26.9	5.05	1.66	9.40	2	21.4	6.02	1.65	9.57	2
pentadecanoic acid	C15:0	2.98	1.21	1.33	3.31	6	3.34	1.18	1.32	3.35	8	3.10	0.96	1.35	3.31	10	3.02	1.26	1.48	2.75	11
hexadecanoic acid	C16:0	106	62.9	1.41	7.67	0	109	73.1	0.97	7.68	0	103	72.5	1.00	7.65	0	108	77.3	1.09	7.72	0
heptadecanoic acid	C17:0	3.03	0.82	1.43	2.49	29	2.06	0.84	1.15	2.46	25	2.20	0.98	1.29	2.48	30	2.51	0.91	1.49	2.48	26
octadecanoic acid	C18:0	84.8	24.5	1.69	14.5	0	62.6	32.1	1.16	14.1	2	62.2	40.7	1.05	13.4	0	59.9	29.4	1.22	14.1	0
Subtotal		249	112	1.30			234	121	1.00			233	153	1.03			223	128	1.06		
Sterols and methoxyphenols																					
cholesterol	Cho	0.73	0.58	0.98	3.19	27	0.77	0.59	0.79	3.78	31	0.78	0.57	0.91	3.85	33	0.65	0.53	0.76	3.76	26
stigmasterol	Sti	0.84	0.79	0.78	16.2	14	1.00	0.78	0.83	19.0	12	0.87	0.76	0.85	16.0	16	0.86	0.75	0.71	19.4	6
acetovanillone	Ace	0.98	0.27	1.65	14.0	13	1.18	0.88	1.10	16.0	12	0.65	0.32	1.26	12.6	14	0.55	0.35	1.15	13.0	11
vanillin	Van	6.03	2.35	1.32	14.3	0	9.25	3.00	1.27	15.8	2	4.84	1.95	1.25	13.2	0	4.67	2.10	1.34	14.2	2
syringaldehyde	Syr	3.55	1.21	2.41	11.9	5	8.68	2.59	2.21	11.1	2	2.69	1.09	2.10	11.5	3	4.64	1.89	1.82	9.33	2
coniferaldehyde	Con	5.91	1.10	2.86	10.6	16	7.73	1.85	2.05	10.8	12	3.60	1.05	2.08	10.1	14	5.20	1.24	2.22	9.92	13
acetosyringone	Ace	0.30	0.10	2.13	6.02	25	0.77	0.18	2.44	8.75	14	0.30	0.11	1.72	6.26	22	0.45	0.13	2.32	5.65	19
Subtotal		18.3	8.36	1.88			29.4	12.2	1.54			13.7	7.15	1.36			17.0	8.15	1.47		
Bulk species (μg m^{-3})																					
EC		0.31	0.27	0.61	2.20	21	0.32	0.29	0.61	2.18	12	0.66	0.54	0.69	4.09	3	0.48	0.44	0.62	3.67	3
OC		3.03	2.87	0.53	10.2	0	3.39	3.10	0.59	10.9	0	3.56	3.34	0.55	11.2	0	3.51	3.40	0.47	11.9	0
PM2.5		6.51	6.20	0.57	3.90	8	6.81	6.61	0.53	4.27	7	9.32	8.39	0.50	5.55	3	7.79	7.48	0.47	6.37	0

Table S3

Statistics for $PM_{2.5}$ components derived from bi-weekly pairs of co-located samples at PAL (July 13, 2004- September 20, 2005).

Molecular marker	Primary (*N*=31)					Duplicate (*N*=31)					*r* [b]	COD[c]
(ng m^{-3})	Mean	SD[a]	Median	S/N	BDL %	Mean	SD	Median	S/N	BDL %		
n-Alkanes												
C22	1.86	1.69	1.32	14.8	0	1.4.0	1.27	1.1.0	14.0	0	0.97	0.16
C23	2.22	1.60	1.71	12.2	0	1.91	1.67	1.55	12.3	0	0.87	0.16
C24	1.32	0.97	1.12	8.22	0	1.23	0.84	1.04	8.07	0	0.85	0.20
C25	1.57	0.96	1.38	10.4	0	1.46	0.84	1.21	10.4	0	0.88	0.16
C26	0.90	0.60	0.83	12.4	0	0.81	0.52	0.63	11.7	3	0.90	0.17
C27	1.10	0.65	0.96	17.6	0	1.01	0.54	0.82	17.0	0	0.87	0.15
C28	0.78	0.64	0.45	18.5	0	0.7	0.54	0.43	16.5	0	0.90	0.18
C29	1.60	1.01	1.48	11.9	0	1.56	1.00	1.38	11.2	0	0.85	0.17
C30	0.68	0.59	0.36	6.80	10	0.63	0.52	0.39	5.87	13	0.89	0.17
C31	2.25	2.42	1.65	1.45	29	2.26	2.35	1.42	1.37	29	0.85	0.19
C32	0.16	0.15	0.09	0.14	94	0.40	0.32	0.42	0.40	45	0.43	0.43
C33	0.43	0.37	0.32	5.36	0	0.79	0.52	0.84	7.21	0	0.53	0.42
C34	0.27	0.21	0.21	5.98	3	0.54	0.40	0.51	8.18	3	0.50	0.41
C35	0.28	0.22	0.22	7.69	6	0.56	0.42	0.56	9.07	0	0.56	0.42
Subtotal	15.4	8.79	14.0			15.2	7.63	15.0				
PAHs												
Flu	0.22	0.22	0.13	5.43	0	0.16	0.13	0.10	4.88	0	0.82	0.29
Pyr	0.18	0.20	0.07	6.02	0	0.13	0.13	0.06	5.36	0	0.90	0.29
BghiF	0.13	0.16	0.05	9.52	0	0.09	0.10	0.05	9.43	0	0.94	0.25
C-pyr	0.06	0.09	0.02	9.44	6	0.04	0.04	0.02	8.95	23	0.92	0.28
BaA	0.11	0.15	0.03	11.7	10	0.07	0.08	0.04	11.0	6	0.91	0.26
CT	0.28	0.35	0.13	20.5	0	0.22	0.24	0.11	19.9	0	0.94	0.27
BbkF	0.34	0.42	0.14	10.6	0	0.24	0.25	0.13	9.63	0	0.93	0.25
BaeP	0.31	0.41	0.11	12.0	3	0.21	0.25	0.09	10.7	0	0.92	0.27
IP	0.09	0.09	0.04	11.4	0	0.08	0.09	0.04	12.0	3	0.96	0.17
BP	0.21	0.21	0.09	19.7	0	0.19	0.2	0.12	19.7	0	0.96	0.16
Cor	0.15	0.17	0.05	3.27	3	0.15	0.16	0.07	3.36	3	0.95	0.16
2M-Flu	0.27	0.35	0.12	6.74	0	0.18	0.21	0.09	5.51	0	0.92	0.25
M-202	0.86	1.15	0.28	6.18	0	0.59	0.72	0.23	5.97	0	0.92	0.25
Ret	0.57	0.92	0.11	5.61	19	0.39	0.64	0.11	5.17	13	0.97	0.32
Sub total	3.48	4.36	1.18			2.55	2.87	1.07				
Oxy-PAHs												
Flu-O	0.69	0.87	0.38	1.68	39	0.32	0.28	0.23	0.87	45	0.76	0.32
Phe-O	0.73	0.62	0.55	7.07	3	0.46	0.48	0.36	6.62	13	0.80	0.24
Xan	0.26	0.16	0.20	8.35	10	0.24	0.15	0.19	8.61	13	0.72	0.34
Nap-DO	0.49	0.30	0.43	7.46	0	0.44	0.29	0.38	7.35	0	0.59	0.25
Ant-DO	0.53	0.34	0.44	7.41	3	0.51	0.32	0.42	8.19	6	0.56	0.29
BaA-O	0.12	0.15	0.05	18.4	3	0.09	0.09	0.05	17.9	3	0.95	0.23
Subtotal	2.73	1.69	2.36			1.93	0.92	1.91				

[a] standard deviation; [b] correlation coefficient; [c] coefficient of divergence.

Table S3 (*continued*)

Molecular marker	Primary (*N*=31)					Duplicate (*N*=31)					*r*	COD
(ng m^{-3})	Mean	SD	Median	S/N	BDL %	Mean	SD	Median	S/N	BDL %		
Steranes												
27-RS-C	0.30	0.38	0.15	12.3	0	0.33	0.41	0.15	12.1	0	0.86	0.21
28-RS-M	0.24	0.35	0.11	10.8	0	0.24	0.33	0.09	10.8	0	0.91	0.23
29-RS-E	0.24	0.33	0.11	16.7	0	0.25	0.30	0.09	16.2	0	0.90	0.21
TS	0.15	0.16	0.08	17.5	0	0.16	0.16	0.08	16.9	0	0.91	0.17
ba-N	0.65	0.89	0.33	13.8	0	0.65	0.84	0.26	13.6	0	0.94	0.18
ab-H	0.48	0.71	0.17	13.8	0	0.50	0.67	0.20	13.6	0	0.94	0.18
31abS	0.21	0.29	0.10	14.2	0	0.21	0.28	0.08	13.8	0	0.91	0.19
31abR	0.15	0.23	0.06	14.0	0	0.16	0.21	0.06	13.5	0	0.94	0.18
32abS	0.12	0.17	0.05	13.6	0	0.13	0.17	0.06	13.4	0	0.91	0.20
32abR	0.09	0.12	0.05	13.0	0	0.10	0.12	0.04	13.0	0	0.90	0.21
subtotal	2.64	3.62	1.28			2.71	3.46	1.05				
n-alkanoic acids												
C12:0	8.92	12.0	4.47	6.50	0	6.47	5.27	4.73	6.27	3	0.59	0.35
C13:0	1.43	1.30	0.94	3.10	35	1.14	1.07	0.64	2.65	55	0.28	0.38
C14:0	9.9	8.39	7.52	6.25	0	7.14	5.14	6.40	5.32	10	0.60	0.33
C15:0	2.26	1.70	1.81	6.01	0	1.43	0.84	1.34	4.67	10	0.53	0.34
C16:0	35.2	27.7	28.0	6.10	3	23.3	14.6	20.5	4.98	3	0.54	0.31
C17:0	1.81	1.70	1.40	2.98	3	1.09	0.71	0.91	2.78	10	0.49	0.34
C18:0	18.7	17.7	16.4	5.25	0	11.4	8.37	8.85	4.34	6	0.59	0.33
Subtotal	77.7	62.6	62.6			51.3	31.0	42.6				
Sterols and methoxyphenols												
Cho	0.84	0.99	0.42	3.62	48	0.92	1.16	0.27	3.75	61	0.68	0.46
Sti	1.02	1.11	0.43	2.43	32	1.06	1.10	0.30	2.57	35	0.71	0.30
Acv	1.67	2.23	0.95	3.98	48	1.35	1.49	0.82	4.07	45	0.93	0.38
Van	4.14	5.20	1.24	3.58	16	2.62	3.47	1.47	3.29	16	0.86	0.37
Syr	4.53	5.61	2.25	8.10	42	3.43	3.23	2.35	8.53	45	0.55	0.38
Con	4.52	5.08	1.89	8.68	29	3.36	3.46	2.25	8.59	39	0.76	0.44
Acs	1.17	1.49	0.52	3.02	45	0.78	0.92	0.28	2.22	52	0.89	0.43
Subtotal	13.7	17.7	3.50			9.74	12.4	3.20				
Bulk species (µg m^{-3})												
EC	0.69	0.42	0.53	7.88	0	0.68	0.41	0.56	7.80	0	0.92	0.14
OC	3.07	1.17	3.04	9.14	0	3.09	1.22	2.98	9.17	0	0.92	0.10

Table S4

Simulated effect of quantification uncertainty on *r* and COD statistics for side-by-side and multi-site comparisons. Asterisks denote simulated values without quantification uncertainties.

Species	Side-by-side					PAL vs. EDI				
	r		COD		Average S/N[a]	*r*		COD		Average S/N[b]
	(X_f*, X_h*)	(X_f, X_h)	(X_f*, X_h*)	(X_f, X_h)		(X_f*, X_h*)	(X_f, X_h)	(X_f*, X_h*)	(X_f, X_h)	
C29	0.87	0.85	0.14	0.16	11.6	0.94	0.93	0.16	0.17	13.6
C32	N.A.[c]	N.A.	N.A.	N.A.	0.27	0.37	0.33	0.38	0.40	3.99
BbkF	0.94	0.93	0.18	0.19	10.1	0.53	0.53	0.40	0.41	15.1
IP	0.97	0.96	0.11	0.13	11.7	0.54	0.52	0.34	0.34	8.06
Nap-DO	0.63	0.60	0.23	0.25	7.40	0.79	0.79	0.28	0.28	18.8
Ant-DO	0.60	0.57	0.25	0.27	7.80	0.79	0.79	0.26	0.26	19.0
ba-N	0.95	0.94	0.13	0.14	13.7	0.69	0.68	0.28	0.29	18.4
ab-H	0.94	0.94	0.14	0.15	13.7	0.76	0.76	0.26	0.26	14.4
C12:0	0.62	0.59	0.32	0.34	6.39	0.81	0.80	0.29	0.30	10.4
C13:0	0.36	0.28	0.40	0.67	2.88	0.72	0.72	0.33	0.33	8.05
C16:0	0.58	0.54	0.32	0.34	5.54	0.72	0.70	0.34	0.35	7.67
C17:0[d]	0.63	0.49	0.33	0.82	2.88	0.72	0.65	0.34	0.47	2.48
Cho	0.74	0.68	0.34	0.48	3.69	0.67	0.60	0.36	0.41	3.49
Van	0.95	0.86	0.21	0.30	3.44	0.76	0.75	0.33	0.33	15.0
EC[d]	0.96	0.92	0.08	0.12	7.84	0.83	0.63	0.17	0.31	2.19
OC	0.99	0.92	0.04	0.09	9.16	0.88	0.85	0.13	0.15	10.5

[a] average signal to noise ratios of side-by-side samples; [b] average signal to noise ratios of the PAL and EDI sites; [c] not available, simulated *r* and COD without quantification uncertainties cannot be obtained due to the extremely low S/N ratio; [d] standard deviation of m_i (random number from a normal distribution with a mean of 0 and standard deviation of 1) was decreased to 0.7 to obtain simulated *r* and COD without quantification uncertainties between PAL and EDI.

Discussion S1. Impact of quantification uncertainty on correlation coefficient (r) and COD

Simulated data were used to evaluate the effect of quantification uncertainty on the values of *r* and COD observed in this study. As mentioned in section *2.3* of the manuscript, the uncertainty is composed of those in instrumental analysis, blank correction and sample air volume, and expressed as S/N ratios in Tables S2 and S3. For this analysis, pairs of bivariate lognormal random variables (X_f*, X_h*) were generated (N = 10^6) with specified correlation coefficients (ρ*), simulating the *true* concentrations of a given species in side-by-side samples or at two sampling sites. To most effectively mimic our study, X_f* and X_h* were generated such that the means and variances of Ln(X_f*) and Ln(X_h*) were estimated from the time series concentrations observed for the DASH study. Simulated *measured* concentrations including quantification uncertainty were then calculated as $x_i = x_i^* + u_i \times m_i$, where x_i* is an element of the true concentration vector X_f*or X_h*; u_i is the quantification uncertainty, which is estimated by the ratio of x_i* to S/N (signal to noise ratio, Table S2 and S3); and m_i is a random number from a normal distribution with a mean of 0 and standard deviation of 1. Values of the correlation coefficient (ρ) and COD are then calculated from the new pair of bivariate variables (X_f, X_h). This process is repeated with a range of values of ρ* until the correlation coefficient (ρ) between X_f and X_h matches the observed value of *r* within ± 0.5%. The percentage differences between ρ* and ρ, and between the CODs of (X_f*, X_h*) and (X_f, X_h), were used to estimate the sensitivity of these statistics to quantification uncertainty.

Table S4 shows the results for 16 species with different quantification uncertainties. For the side-by-side samples, the effect on the statistics is generally greatest for those species with the lowest signal to noise ratios (e.g., tridecanoic acid, heptadecanoic acid), supporting the hypothesis that quantification uncertainties contribute significantly to the high side-by-side

divergence observed for some species. On a relative basis, quantification uncertainty also contributes significantly to the divergence in side-by-side measurements of bulk EC and OC, although their absolute coefficients of divergence are low (COD = 0.14 and 0.10; Table S3). However, the estimated quantification uncertainties do not account for all of the observed divergence in the side-by-side measurements, suggesting there are unaccounted for differences between the samplers or the air parcels being sampled. The influence of quantification uncertainty on comparisons across locations is illustrated in Table S4 with results for PAL and EDI. For the multi-site comparisons, species with higher quantification uncertainty (lower S/N ratio) show higher influence of quantification uncertainty on *r* and COD. The COD value for EC is also highly impacted, on a relative basis. Thus large uncertainties in species quantification can have an impact on the assessment of spatial variability using *r* and COD. The simulation approach demonstrated here may be useful for understanding the impact of quantification uncertainties on cross-site comparisons in other studies where side-by-side measurements are not available for comparison.

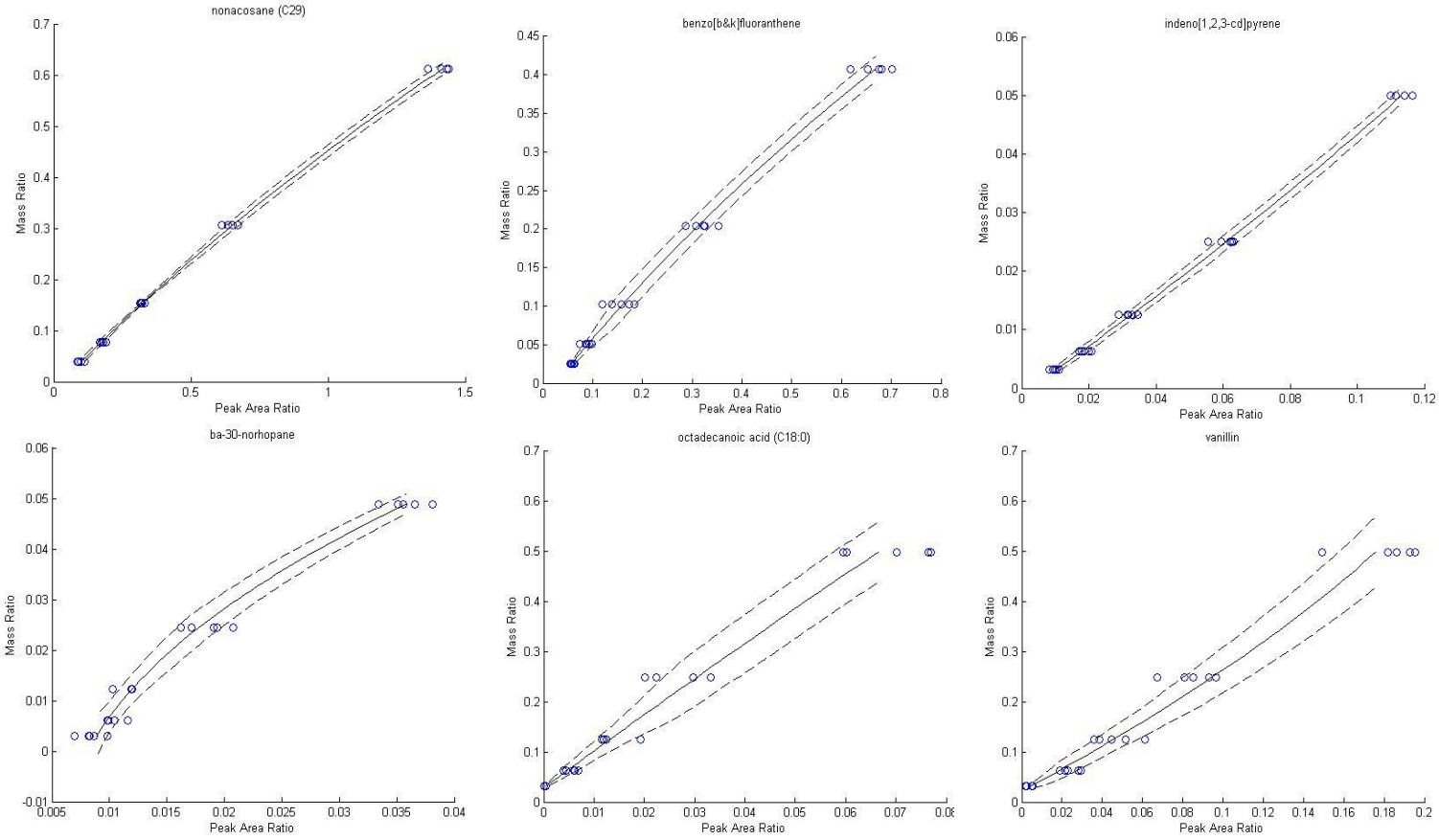
Figure Captions

Figure S1 – Calibration curves for selected species from one of the three quantification batches.

Figure S2 – Concentrations of different groups of $PM_{2.5}$ species on November 25th 2008 (black triangles) vs. annual averages (bar plots).

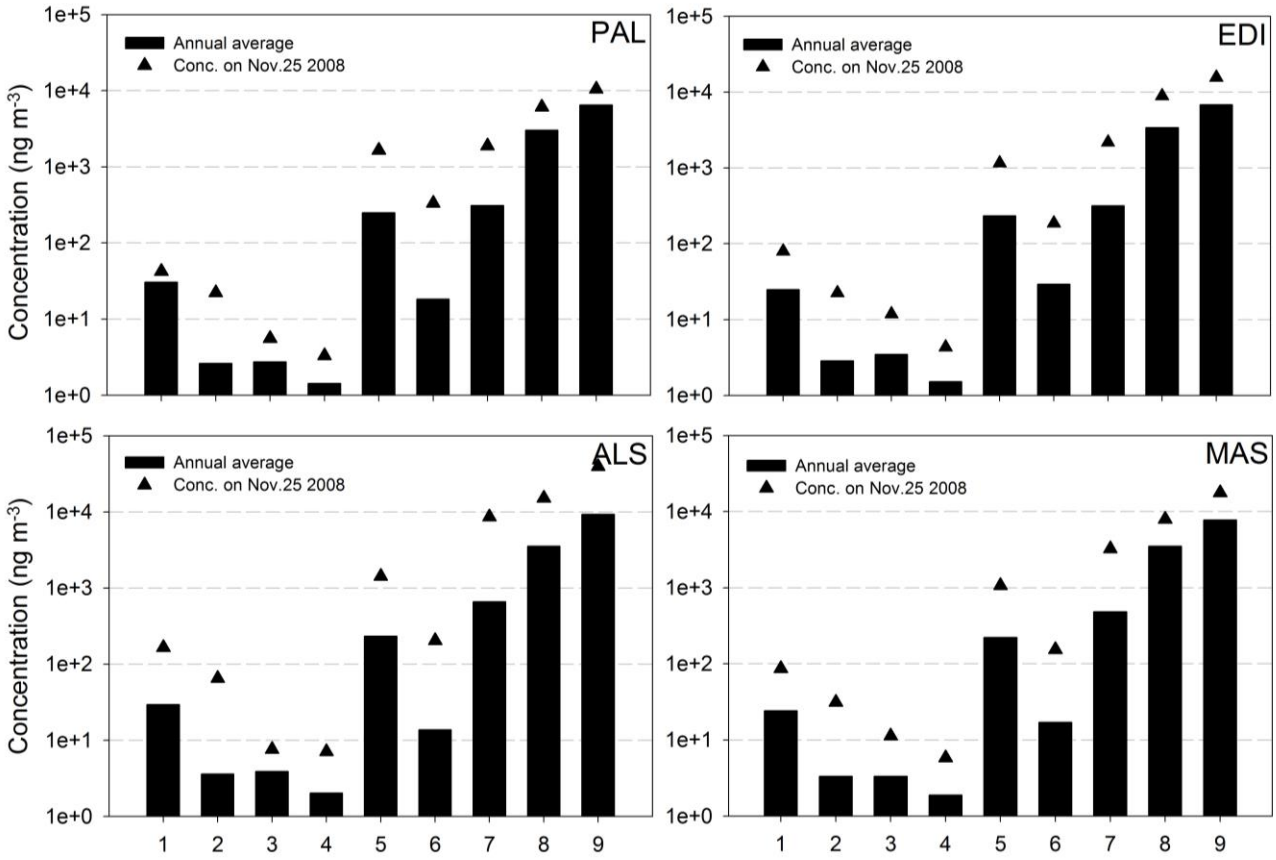
Figure S3 – Hourly observations for (a) CO, (b) NO_X, (c) CO/NO_X ratios, (d) wind speed, (e) ambient temperature on November 25, 2008 (red diamond) vs. annual distribution data (box plots). The boxes depict the median (black line), inner quartile range (gray box), 10th and 90th percentiles (whiskers) and mean (light blue circle).

Figure S1



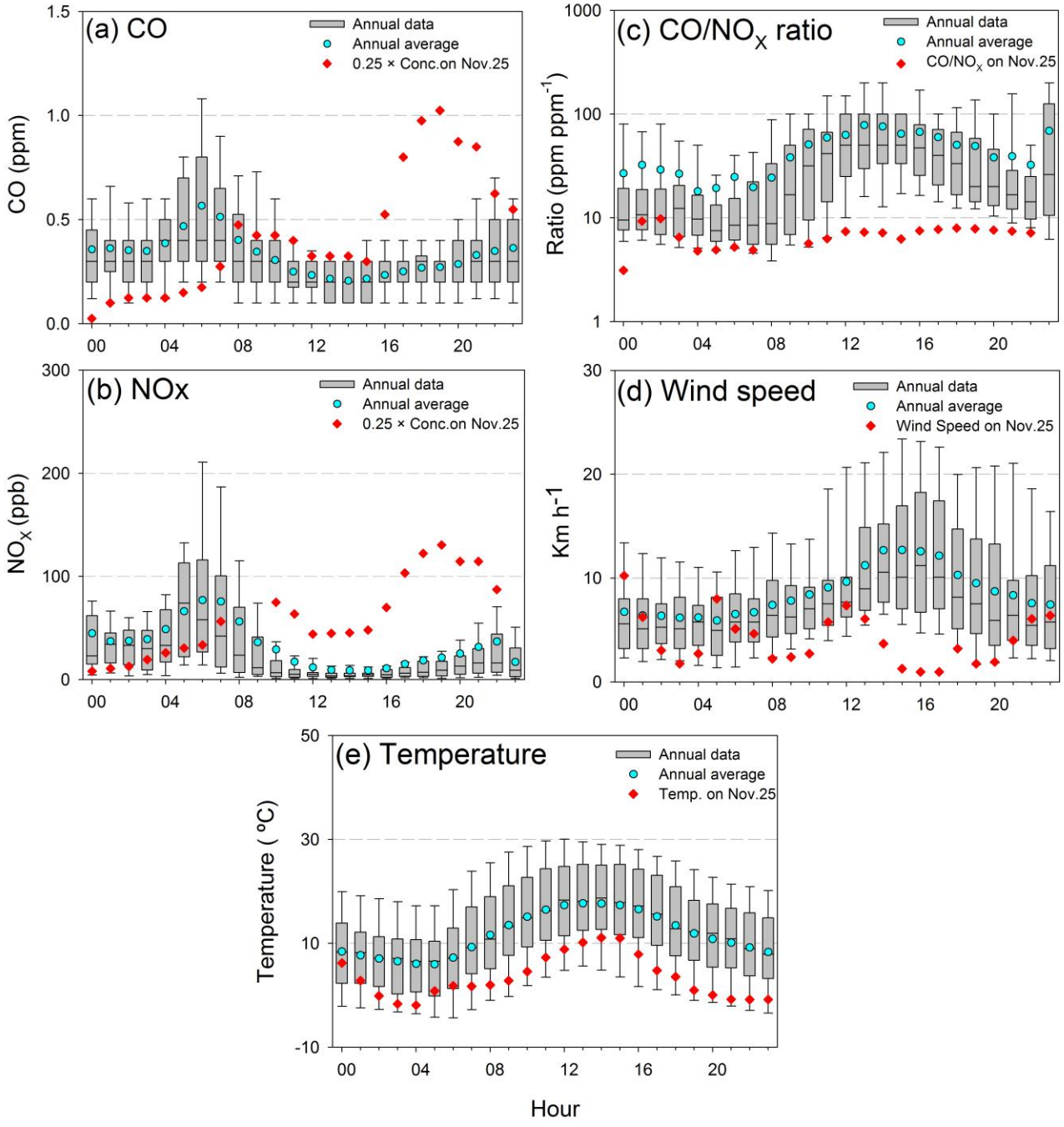
The six plots above are calibration curves used for quantification, which determines the final mass amount of each molecular maker by converting peak area ratios to mass ratios. The dashed lines represent uncertainties associated with mass ratios that correspond to the peak area ratios of each compound in samples. For measurements below the range covered by the quantification standard dilutions, the calibration curve was extrapolated linearly through zero, and the absolute uncertainty was extrapolated down. While for the measurements above the range of quantification standard dilutions, the calibration curve was extrapolated upward by following the slope at the top end of the quadratic calibration curve, and the relative uncertainty was extrapolated up (Dutton et al., 2009).

Figure S2



1. *n*-alkanes; 2. PAHs; 3. Oxy-PAHs; 4. Steranes; 5 *n*-alkanoic acids; 6. Sterols and Methoxyphenols; 7.EC; 8. OC; 9. $PM_{2.5}$ mass

Figure S3


(a) CO
Annual data
Annual average
0.25 × Conc.on Nov.25
CO (ppm)
(b) NOx
NO$_X$ (ppb)
(c) CO/NO$_X$ ratio
CO/NO$_X$ on Nov.25
Ratio (ppm ppm^{-1})
(d) Wind speed
Wind Speed on Nov.25
Km h^{-1}
(e) Temperature
Temp. on Nov.25
Temperature (°C)
Hour

Discussion S2. Extreme spike during Thanksgiving holiday

The compositional data of samples collected on November 25th 2008, two days before Thanksgiving Day, were compared with annual averages in Figure S2, from which we can observe a pronounced increase in all groups of species. The OC/EC ratios over the four sampling sites on that day were 1.6 - 4.0, 2 - 3 times lower than their corresponding annual averages, suggesting a sharp increase of contribution from primary emissions.

In order to find a plausible explanation for this spike, hourly CO and NO_X mixing ratios as well as wind speed and temperature measured at the Welby site were obtained from the Colorado Department of Public Health and Environment (CDPHE). The Welby station is located 1 mile northwest of ALS. On Nov. 25th 2008, mixing ratios of CO and NO_X are much higher than on other sampling days, with peaks occurring in the late morning and early evening (Figure S3a, b). CO/NOx ratios lie between 3.1 and 9.8 (average 6.8) with little variation after 4:00 am (Figure S3c). This ratio is much lower than the annual average and closer to the value for traffic emissions (8.8 - 9.4 ppm ppm^{-1}) (Kirchstetter et al., 1999) than that for smoke from burning various prescribed biomass fuels (> 17 ppm ppm^{-1}) (Andreae and Merlet, 2001) and wildfire (> 34 ppm ppm^{-1}) (Ward et al., 1992), suggesting a stronger motor vehicle contribution on that day. In addition, wind speeds on Nov.25th 2008 were lower than annual averages during most time of the day (Figure S3d). Hourly average wind speeds were negatively correlated with concentrations of CO (r = 0.42) and NO_X (r = 0.45). Ambient temperature exhibited similar hourly variations as on other sampling days with lower values (Figure S3e). As a result, the unusual extreme spike during the Thanksgiving holiday was likely initiated by heavy traffic activity in the late morning, emitting a large amount of pollution that accumulated in a stagnant and cold atmosphere, and then was enhanced by more vehicle emissions and residential wood

combustions in the evening. A body of evidence developed in the past shows increased daily mortality and morbidity associated with exposures to fine particulate air pollution (Dockery, 2001; de Hartog et al., 2008), thus a sudden acute increase in $PM_{2.5}$ mass and the related components as observed in this study might pose a threat to public health in a short term.

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