

Supplementary Information for
Depletion of gaseous polycyclic aromatic hydrocarbons by a forest canopy

S.-D. Choi¹, R. M. Staebler², H. Li^{1,*}, Y. Su^{1,**}, B. Gevao^{1,***}, T. Harner², F. Wania¹

¹Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, ON, Canada, M1C 1A4

²Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada, M3H 5T4

*now at: Worsfold Water Quality Centre, Trent University, Peterborough, Ontario, Canada, K9J 7B8

**now at: Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada, M3H 5T4

***now at: Department of Environmental Science, Environment and Urban Development Division, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait

Correspondence to: F. Wania (frank.wania@utoronto.ca).

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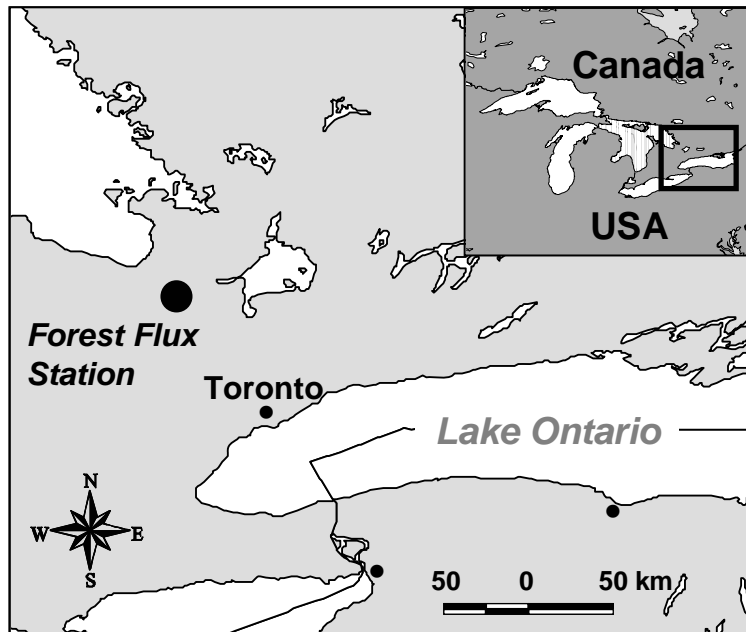


Fig. S1 Location of the forest flux station at Borden, Ontario, Canada.

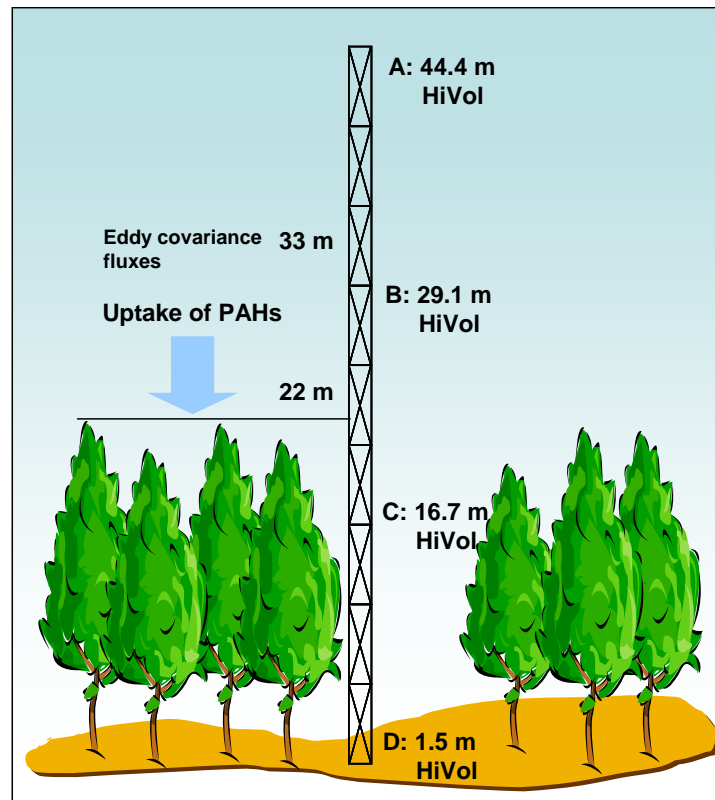


Fig. S2 High volume air sampling at different heights (A: 44.4 m, B: 29.1 m, C: 16.7 m, and D: 1.5 m) on a 45-m scaffold tower. Eddy covariance fluxes were measured at 33 m. Average canopy height is 22 m.

Table S1. Air sampling time (local time) and mean temperature (°C) for 12 sampling events

Event	Start time	End time	Average temperature
1	12:49pm (April 24)	2:54pm (April 25)	4.6
2	3:04pm (April 25)	3:00pm (April 26)	4.8
3	6:23pm (May 06)	6:11pm (May 07)	8.2
4	2:32pm (May 09)	3:02pm (May 10)	13.0
5	4:48pm (May 12)	5:08pm (May 13)	6.0
6	6:25pm (May 16)	6:25pm (May 17)	11.6
7	2:40pm (May 18)	2:48pm (May 19)	15.9
8	2:10pm (May 21)	6:52pm (May 22)	9.0
9	6:52pm (May 24)	6:19pm (May 25)	10.2
10	4:34pm (May 27)	4:59pm (May 28)	11.7
11	5:38pm (May 30)	4:56pm (May 31)	10.7
12	4:49pm (June 02)	6:16pm (June 03)	12.0

GC Temperature Program and Target Ions. The GC oven temperature program was as follows: initial temperature held at 80°C for 1 min, increased at 10°·min⁻¹ to 90°C, held 1 min, 4°·min⁻¹ to 130°C, 5 °C·min⁻¹ to 240°C, 4 °C·min⁻¹ to 265°C and held 16 min, then 10°·min⁻¹ to 280°C and held 15 min. The interface connecting the MSD was set to temperature of 280°C, while the ion source and quadrupole temperatures were 230°C and 150°C, respectively. Ions used for SIM of target compounds were (target/qualifier): naphthalene (128/127); d₈-naphthalene(136/137); acenaphthylene (152/151); d₈-acenaphthylene(160/159); acenaphthene (153/154); fluorene (166/165); phenanthrene (178/179); d₁₀-phenanthrene (188/189); anthracene (178/179); fluoranthene (202/200); d₁₀-fluoranthene(212/213); pyrene (202/200); d₁₀-pyrene (212/213); benz(a)anthracene (228/226); chrysene (228/226); benzo(b)fluoranthene (252/253); benzo(k)-fluoranthene (252/253); benzo(a)pyrene (252/253); d₁₂-benzo(a)pyrene (264/265); indeno-(123,cd)pyrene (276/274); dibenz(a,h)anthracene (278/276); benzo(g,h,i)perylene (276/274); d₁₂-benzo(ghi)perylene (288/289); mirex (272/237).

Table S2. Average method detection limits (MDL) for 13 selected PAHs and average recoveries for 7 deuterated PAHs

	MDL (pg·m ⁻³)			Recovery (%)	
	PUF	GFF		PUF	GFF
Fluorene	10.7	1.51	D ₈ -Naphthalene	74	74
Phenanthrene	27.1	6.51	D ₈ -Acenaphthylene	95	99
Anthracene	3.4	0.14	D ₁₀ -Phenanthrene	120	154
Fluoranthene	23.4	0.05	D ₁₀ -Fluoranthene	130	127
Pyrene	20.4	0.08	D ₁₀ -Pyrene	136	120
Benz(a)anthracene	0.10	0.10	D ₁₂ -Benzo(a)pyrene	93	108
Chrysene	0.09	0.09	D ₁₂ -Benzo(ghi)perylene	65	122
Benzo(b)fluoranthene	0.21	0.21			
Benzo(k)fluoranthene	0.22	0.22			
Benzo(a)pyrene	0.76	0.76			
Indeno(123,cd)pyrene	0.26	0.26			
Dibenz(ah)anthracene	0.39	0.39			
Benzo(ghi)perylene	0.23	0.23			

Table S3. Concentrations of 13 PAHs in the gas phase for 12 sampling events. BDL indicates below method detection limit

Event	Height	(pg·m ⁻³)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
1	A	489	1227	105	126	116	3.6	5.8	3.0	BDL	BDL	2.2	BDL	3.8
	B	567	966	38	120	38	1.2	1.8	0.5	BDL	BDL	BDL	BDL	0.4
	C	571	862	11	173	82	6.5	11.7	BDL	BDL	BDL	6.6	BDL	5.1
	D	622	1481	178	131	191	9.1	11.5	BDL	BDL	BDL	5.9	BDL	6.2
2	A	525	1327	85	219	164	3.3	16.3	6.1	BDL	BDL	3.2	BDL	3.2
	B	572	1154	41	304	161	2.1	13.1	5.4	BDL	BDL	BDL	BDL	3.0
	C	575	979	17	187	121	4.3	14.9	6.8	BDL	BDL	4.2	BDL	4.8
	D	509	1155	104	110	132	3.6	9.5	4.8	BDL	BDL	BDL	BDL	3.0
3	A	441	1676	146	250	241	3.1	10.9	2.3	1.0	BDL	BDL	BDL	0.7
	B	380	1815	203	256	211	3.7	12.5	2.5	BDL	BDL	BDL	BDL	0.6
	C	395	1073	21	264	120	3.6	11.7	3.5	BDL	BDL	0.7	BDL	1.0
	D	341	1432	113	199	204	5.0	9.9	2.5	BDL	BDL	0.5	BDL	0.6
4	A	993	2444	216	315	337	5.1	13.9	7.2	2.6	BDL	1.7	BDL	2.2
	B	944	1275	71	275	116	2.7	12.3	1.9	BDL	BDL	BDL	BDL	BDL
	C	771	1008	BDL	305	84	5.1	13.7	10.5	3.6	BDL	5.0	0.8	5.4
	D	677	1905	191	290	260	5.0	11.3	2.9	BDL	BDL	0.7	BDL	1.7
5	A	237	763	83	114	143	2.5	5.9	1.3	BDL	BDL	BDL	BDL	1.2
	B	213	560	45	102	82	2.0	6.5	1.6	BDL	BDL	BDL	BDL	BDL
	C	170	348	12	87	50	2.1	6.3	3.2	BDL	BDL	0.4	BDL	0.5
	D	360	1430	164	140	249	3.0	4.9	1.7	BDL	BDL	0.5	BDL	0.6
6	A	733	1271	71	232	167	1.4	7.6	1.2	BDL	BDL	0.2	BDL	0.3
	B	804	1107	54	164	81	1.3	6.4	1.2	BDL	BDL	BDL	BDL	BDL
	C	815	841	BDL	214	69	2.5	8.8	1.9	BDL	BDL	0.7	BDL	0.8
	D	724	1478	146	169	183	3.4	6.8	2.1	BDL	BDL	0.4	BDL	0.6
7	A	700	2474	224	300	378	6.9	19.0	8.7	3.7	4.8	4.0	0.4	3.4
	B	701	1511	109	289	175	10.9	23.1	8.7	4.3	6.5	6.2	0.6	4.3
	C	818	877	BDL	212	78	4.1	15.3	8.6	4.8	7.5	5.6	0.5	3.7
	D	526	2584	381	129	355	7.3	9.5	7.9	3.2	4.9	4.0	BDL	3.6
8	A	351	991	66	113	142	2.4	5.2	2.0	0.9	BDL	1.1	BDL	1.0
	B	323	604	20	99	51	0.8	3.8	BDL	BDL	BDL	BDL	BDL	BDL
	C	312	523	BDL	94	34	5.5	10.9	2.8	BDL	BDL	1.0	BDL	1.3
	D	307	1171	152	83	158	4.5	5.2	3.5	2.1	BDL	1.1	BDL	1.2

Table S3. Continued

Event	Height	(pg·m ⁻³)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
9	A	501	1741	102	304	301	4.3	19.0	5.0	1.4	0.8	1.0	BDL	1.0
	B	432	885	34	204	115	4.3	12.7	4.4	1.5	BDL	BDL	BDL	BDL
	C	424	799	BDL	188	86	3.7	12.1	5.6	1.4	BDL	1.8	BDL	2.4
	D	419	1138	57	106	133	2.8	6.4	2.4	0.7	BDL	0.3	BDL	0.4
10	A	250	1240	109	114	171	2.3	7.4	2.1	BDL	BDL	BDL	BDL	0.2
	B	256	753	32	114	77	1.7	6.4	1.8	BDL	BDL	BDL	BDL	BDL
	C	129	269	4	93	37	1.7	5.3	1.8	BDL	BDL	BDL	BDL	0.3
	D	261	1659	63	108	238	3.7	5.9	2.3	0.7	BDL	0.4	BDL	0.4
11	A	287	2489	38	437	408	19.6	34.3	14.9	5.7	BDL	1.0	BDL	0.9
	B	239	1310	39	338	189	19.1	26.4	26.1	7.2	BDL	0.8	BDL	0.6
	C	255	1255	15	293	143	17.7	25.1	27.2	8.2	BDL	2.2	BDL	1.8
	D	276	2142	168	257	311	18.7	21.1	22.4	7.9	BDL	1.7	BDL	1.1
12	A	123	1138	76	142	169	4.2	17.1	5.0	BDL	BDL	BDL	BDL	0.6
	B	91	724	37	103	71	4.4	13.8	0.9	BDL	BDL	BDL	BDL	BDL
	C	98	475	5	115	64	6.5	13.5	6.6	BDL	BDL	2.0	BDL	2.0
	D	126	1621	109	122	282	9.8	10.6	5.3	1.1	BDL	0.8	BDL	0.7

Fl=Fluorene, Phe=Phenanthrene, Ant=Anthracene, FA=Fluoranthene, PY=Pyrene,
BaA=Benz(a)anthracene, CR=Chrysene, BbF=Benzo(b)fluoranthene, BkF=Benzo(k)fluoranthene,
BaP=Benzo(a)pyrene, IcdP=Indeno(123,cd)pyrene, DahA=Dibenz(ah)anthracene,
BghiP=Benzo(ghi)perylene

Table S4. Concentrations of 13 PAHs in the particle phase for 12 sampling events. BDL indicates below method detection limit

Event	Height	(pg·m ⁻³)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
1	A	1.3	15.4	4.4	49	43	29	34	48	21	30	37	9	37
	B	1.8	23.5	3.6	72	53	37	61	80	33	30	60	12	54
	C	1.6	24.5	4.8	65	56	40	55	57	29	38	52	11	40
	D	1.3	16.5	4.4	55	55	43	49	50	25	39	44	9	37
2	A	1.3	11.3	3.6	31	29	24	39	54	23	28	43	10	37
	B	1.5	12.6	3.9	39	29	24	42	62	28	30	52	11	43
	C	1.4	9.8	3.5	31	24	20	35	45	23	23	34	9	30
	D	1.3	9.5	3.4	34	26	22	34	49	22	27	43	10	37
3	A	0.9	BDL	3.0	9	8	4	15	16	10	7	13	4	14
	B	1.0	BDL	3.1	15	14	10	16	10	6	3	12	5	13
	C	0.9	BDL	3.0	8	8	5	14	14	5	4	11	2	11
	D	0.8	BDL	BDL	7	7	9	12	13	5	4	11	2	11
4	A	2.0	11.6	3.9	23	23	16	31	53	21	22	32	10	36
	B	2.2	11.0	4.1	29	25	19	40	66	26	28	42	11	44
	C	2.0	8.1	3.9	20	19	17	32	46	19	21	28	9	31
	D	1.9	8.3	3.8	23	23	20	35	57	21	28	42	11	45
5	A	1.4	BDL	BDL	6	6	4	5	3	2	3	6	2	7
	B	BDL	BDL	BDL	4	4	5	5	7	5	3	7	5	7
	C	1.5	BDL	BDL	7	7	4	6	9	2	3	6	BDL	7
	D	1.3	BDL	BDL	6	6	3	5	7	BDL	3	6	BDL	7
6	A	1.8	6.6	3.5	17	16	11	16	20	11	7	18	7	18
	B	1.9	6.5	3.6	17	16	10	15	16	8	5	13	5	14
	C	1.7	8.4	3.6	15	11	9	13	14	6	2	14	5	13
	D	3.8	7.3	BDL	10	14	6	9	11	7	4	10	5	11
7	A	3.6	14.2	BDL	32	28	17	31	47	24	27	39	9	42
	B	3.6	12.9	BDL	28	25	19	34	49	23	25	48	10	46
	C	1.3	8.9	4.3	31	28	24	40	60	28	30	55	11	52
	D	3.3	8.4	BDL	18	21	13	20	47	21	29	44	9	35
8	A	0.8	3.3	BDL	14	14	12	15	25	9	7	18	5	18
	B	0.9	4.5	BDL	15	20	11	17	30	12	14	23	6	23
	C	0.8	6.5	BDL	11	15	9	16	23	10	9	18	5	17
	D	0.7	2.1	BDL	8	7	9	11	16	11	8	12	4	13

Table S4. Continued

Event	Height	(pg·m ⁻³)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
9	A	0.9	BDL	BDL	14	14	7	10	18	10	7	18	6	16
	B	0.9	3.0	BDL	11	10	12	16	24	15	12	22	6	20
	C	0.8	4.6	BDL	5	11	5	6	10	6	4	8	5	8
	D	0.7	4.9	BDL	7	7	6	6	14	8	6	17	5	14
10	A	0.4	3.5	2.1	18	15	6	15	21	10	13	19	6	17
	B	0.4	3.4	1.5	22	16	7	11	17	10	7	15	6	13
	C	0.4	2.7	0.6	15	13	7	11	12	8	5	12	5	10
	D	0.4	BDL	BDL	12	10	8	12	17	10	8	18	5	15
11	A	0.3	BDL	BDL	8	10	5	5	13	8	4	22	6	17
	B	0.3	BDL	1.4	9	6	8	11	26	11	5	43	9	35
	C	3.0	3.7	BDL	5	6	6	7	18	11	6	36	8	28
	D	0.2	3.9	BDL	6	7	6	7	20	12	7	45	10	36
12	A	0.2	BDL	1.4	11	11	15	24	48	23	20	33	10	26
	B	0.3	BDL	1.6	14	15	17	26	45	21	21	39	11	28
	C	0.3	BDL	BDL	12	12	13	20	36	17	16	25	11	20
	D	0.3	BDL	BDL	10	11	9	13	25	11	8	24	7	20

Fl=Fluorene, Phe=Phenanthrene, Ant=Anthracene, FA=Fluoranthene, PY=Pyrene,
BaA=Benz(a)anthracene, CR=Chrysene, BbF=Benzo(b)fluoranthene, BkF=Benzo(k)fluoranthene,
BaP=Benzo(a)pyrene, IcdP=Indeno(123,cd)pyrene, DahA=Dibenz(ah)anthracene,
BghiP=Benzo(ghi)perylene

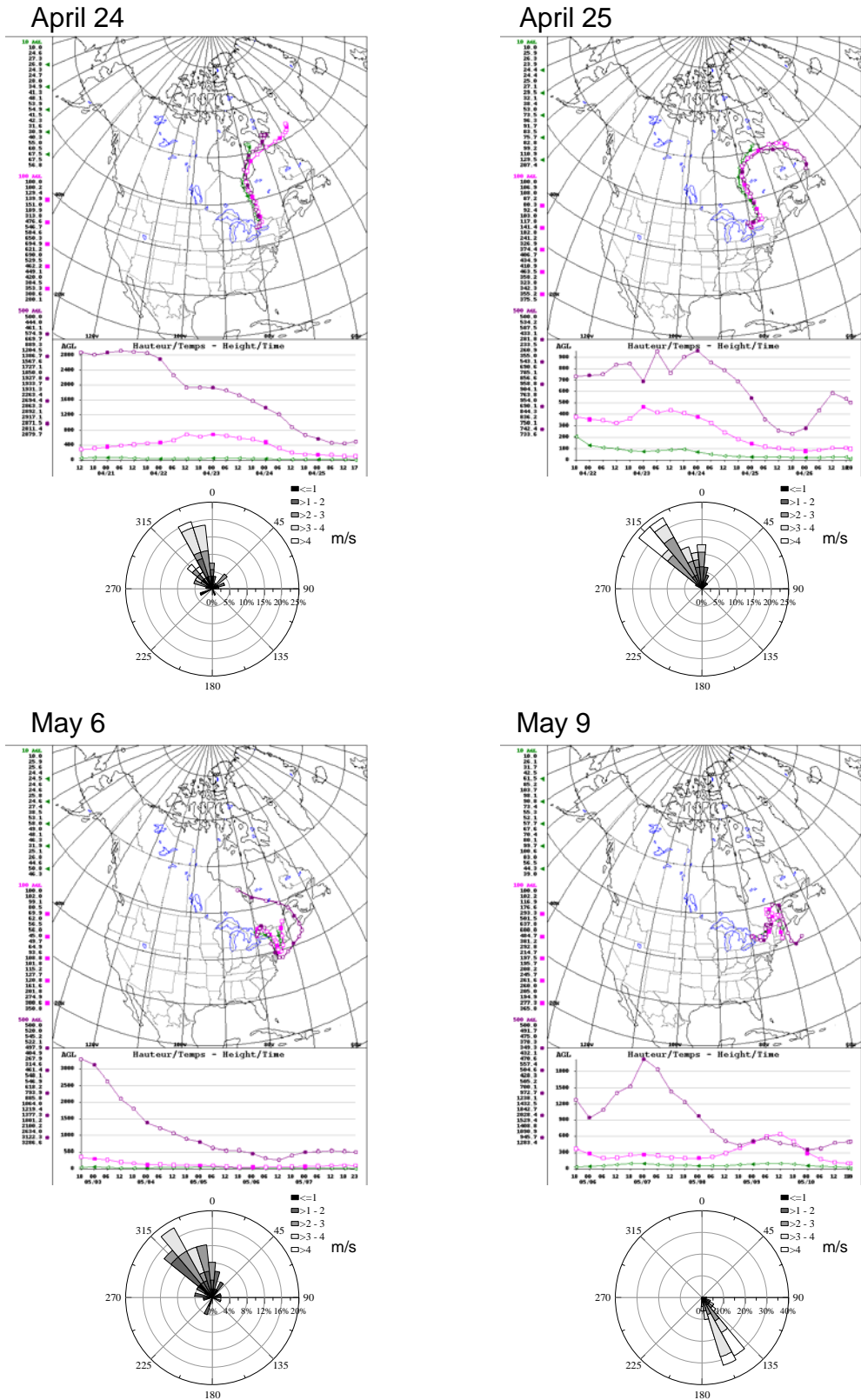
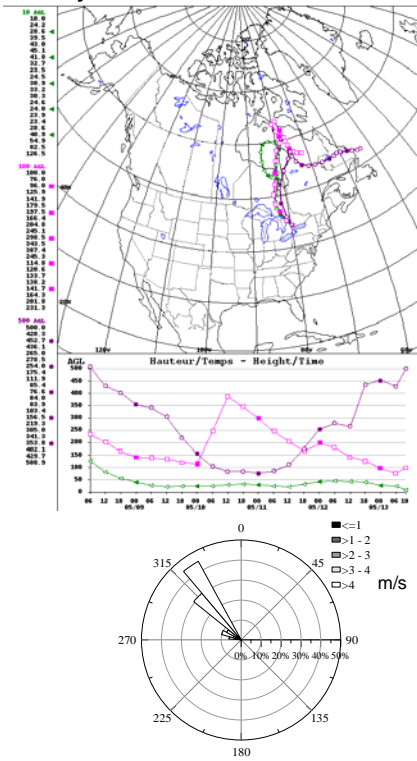
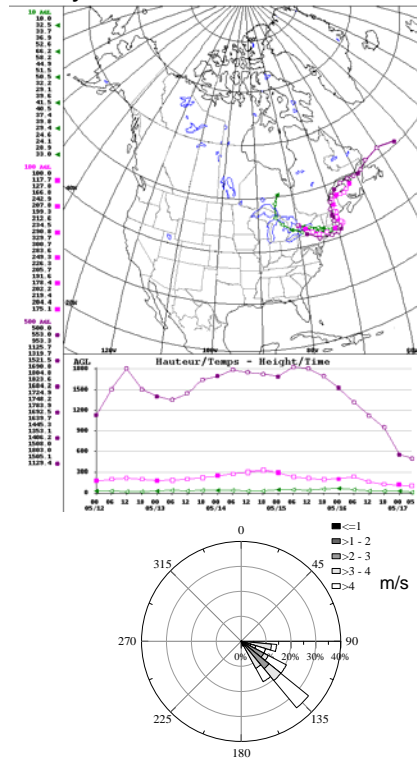


Fig. S3 Five-day back trajectories at three heights (10, 100, 500 m) and wind-rose diagrams during sampling events.

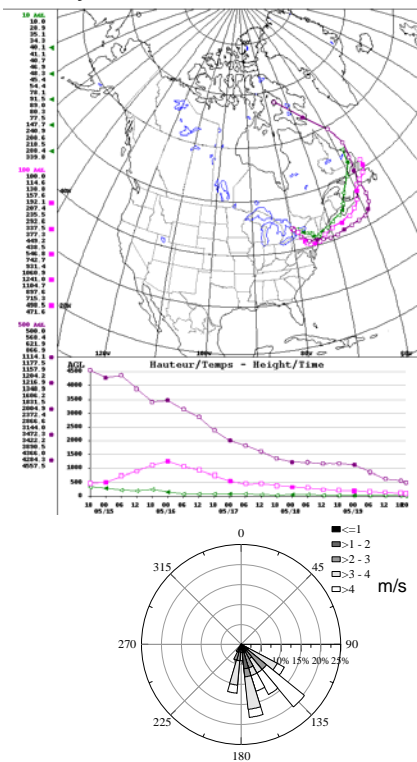
May 12



May 16



May 18



May 21

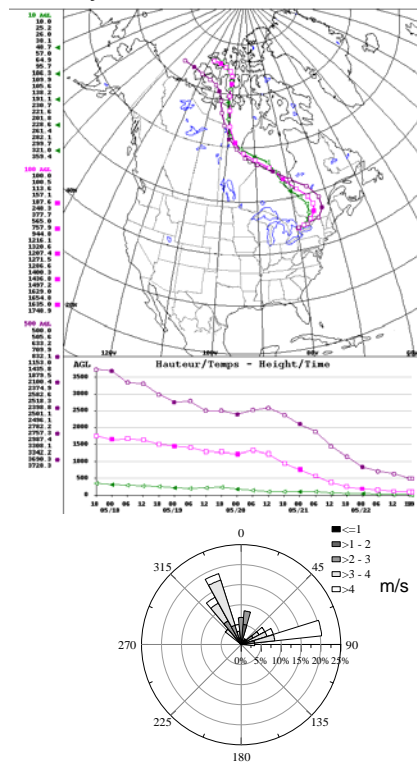
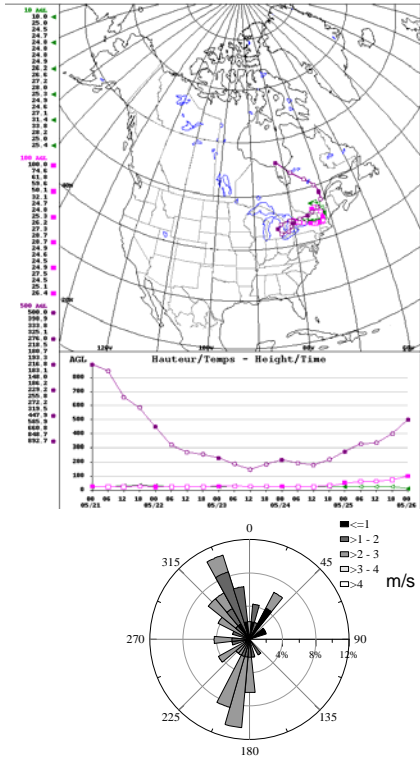
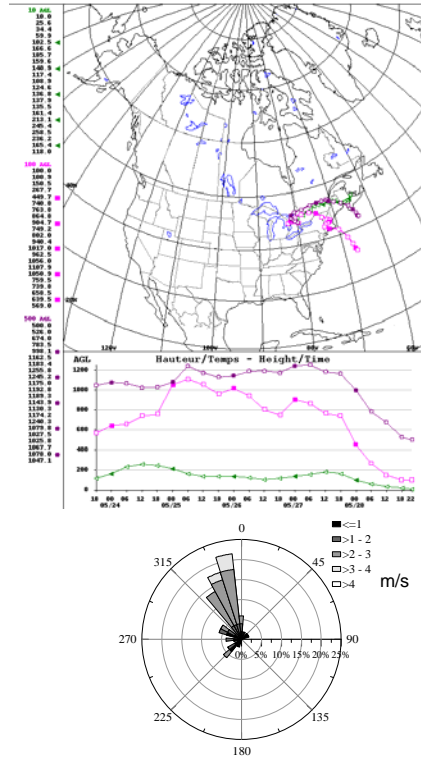


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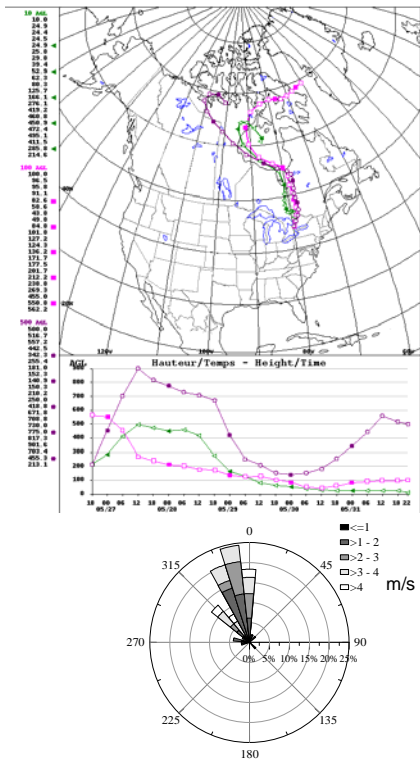
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May 27



May 30



June 2

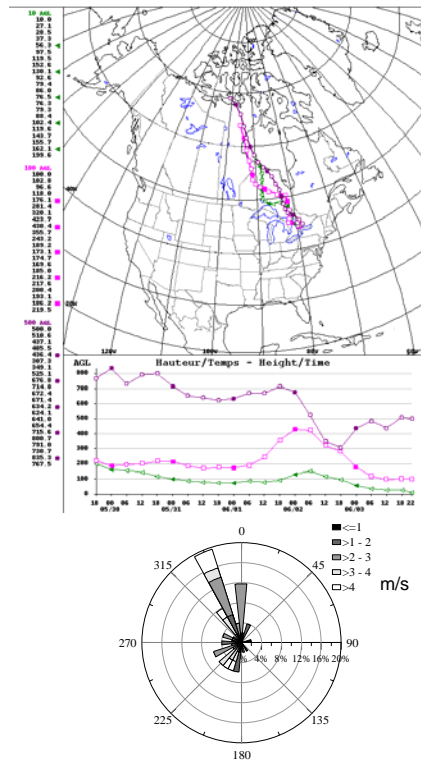


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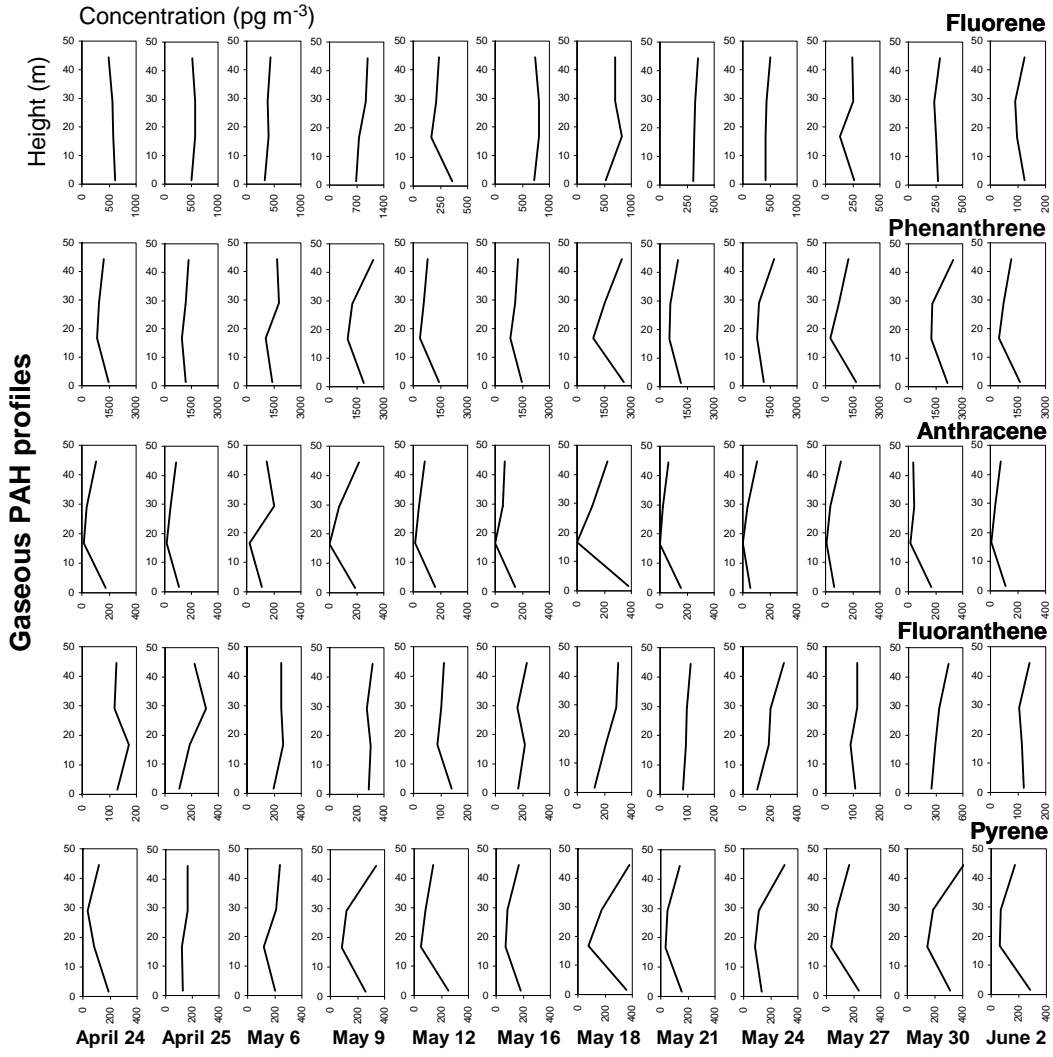


Fig. S4 Vertical profiles of gaseous and particulate PAHs measured at the 4 different heights.

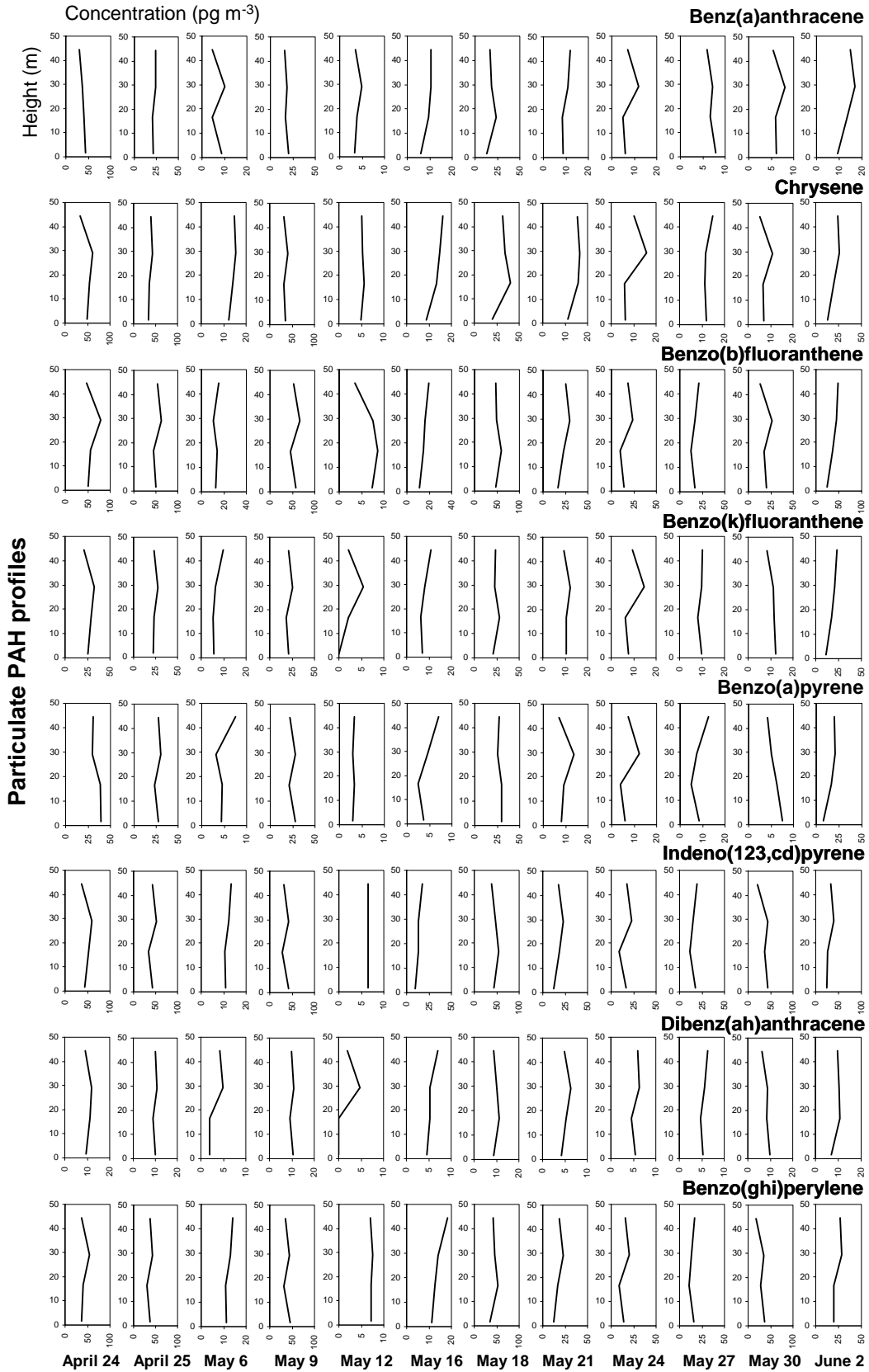


Fig. S4 Continued.

Table S5. Measured particle-bound percentages of 13 PAHs for 12 sampling events

Event	Height	(%)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
1	A	0.3	1.2	4	28	27	89	85	94	100	100	95	100	91
	B	0.3	2.4	9	37	58	97	97	99	100	100	100	100	99
	C	0.3	2.8	31	27	41	86	82	100	100	100	89	100	89
	D	0.2	1.1	2	30	22	83	81	100	100	100	88	100	86
2	A	0.3	0.8	4	13	15	88	70	90	100	100	93	100	92
	B	0.3	1.1	9	11	15	92	76	92	100	100	100	100	94
	C	0.2	1.0	17	14	17	83	70	87	100	100	89	100	86
	D	0.2	0.8	3	23	16	86	78	91	100	100	100	100	93
3	A	0.2	0.0	2	3	3	59	57	87	91	100	100	100	96
	B	0.3	0.0	2	6	6	73	55	81	100	100	100	100	96
	C	0.2	0.0	13	3	6	56	55	80	100	100	93	100	92
	D	0.2	0.0	0	4	3	64	56	84	100	100	96	100	95
4	A	0.2	0.5	2	7	6	76	69	88	89	100	95	100	94
	B	0.2	0.9	6	10	18	87	77	97	100	100	100	100	100
	C	0.3	0.8	100	6	19	77	70	82	84	100	85	92	85
	D	0.3	0.4	2	7	8	80	76	95	100	100	98	100	96
5	A	0.6	0.0	0	5	4	59	46	72	100	100	100	100	85
	B	0.0	0.0	0	4	5	72	45	82	100	100	100	100	100
	C	0.8	0.0	0	7	12	64	47	73	100	100	94	0	94
	D	0.4	0.0	0	4	2	53	50	81	0	100	93	0	92
6	A	0.2	0.5	5	7	9	88	68	94	100	100	99	100	98
	B	0.2	0.6	6	9	16	89	69	93	100	100	100	100	100
	C	0.2	1.0	100	6	13	79	61	89	100	100	95	100	94
	D	0.5	0.5	0	6	7	63	56	84	100	100	96	100	95
7	A	0.5	0.6	0	10	7	71	62	84	86	85	91	96	93
	B	0.5	0.8	0	9	13	63	60	85	84	79	88	94	91
	C	0.2	1.0	100	13	26	85	72	88	85	80	91	96	93
	D	0.6	0.3	0	12	5	64	68	86	87	86	92	100	91
8	A	0.2	0.3	0	11	9	83	75	93	92	100	94	100	95
	B	0.3	0.7	0	13	28	93	82	100	100	100	100	100	100
	C	0.3	1.2	0	11	31	61	59	89	100	100	95	100	93
	D	0.2	0.2	0	8	4	66	68	83	84	100	92	100	91

Table S5. Continued

Event	Height	(%)												
		Fl	Phe	Ant	FA	PY	BaA	CR	BbF	BkF	BaP	IcdP	DahA	BghiP
9	A	0.2	0.0	0	4	5	62	35	79	88	90	95	100	94
	B	0.2	0.3	0	5	8	74	55	84	91	100	100	100	100
	C	0.2	0.6	0	3	11	57	33	63	82	100	82	100	77
	D	0.2	0.4	0	6	5	68	50	85	92	100	98	100	97
10	A	0.2	0.3	2	14	8	72	67	91	100	100	100	100	99
	B	0.2	0.4	4	16	17	81	64	90	100	100	100	100	100
	C	0.3	1.0	14	14	26	80	68	87	100	100	100	100	97
	D	0.1	0.0	0	10	4	68	67	88	94	100	98	100	98
11	A	0.1	0.0	0	2	2	21	13	47	59	100	96	100	95
	B	0.1	0.0	3	3	3	30	29	50	61	100	98	100	98
	C	1.2	0.3	0	2	4	25	21	39	58	100	94	100	94
	D	0.1	0.2	0	2	2	25	25	47	61	100	96	100	97
12	A	0.2	0.0	2	7	6	78	58	91	100	100	100	100	98
	B	0.4	0.0	4	12	18	79	65	98	100	100	100	100	100
	C	0.3	0.0	0	9	16	68	60	84	100	100	93	100	91
	D	0.2	0.0	0	7	4	48	55	82	91	100	97	100	97

Fl=Fluorene, Phe=Phenanthrene, Ant=Anthracene, FA=Fluoranthene, PY=Pyrene,
BaA=Benzo(a)anthracene, CR=Chrysene, BbF=Benzo(b)fluoranthene, BkF=Benzo(k)fluoranthene,
BaP=Benzo(a)pyrene, IcdP=Indeno(123,cd)pyrene, DahA=Dibenz(ah)anthracene,
BghiP=Benzo(ghi)perylene

Gas/Particle Partitioning. Because Fig. 2 indicated that rapid uptake of gaseous PAHs by the forest canopy is expected to affect the gas/particle (G/P) partitioning behavior, this was further explored by relating the fraction in the particle phase (Table S5) to a PAH's vapor pressure. Adopting the approach by Su et al. (2006), the fraction in the particle phase (Φ) was calculated from the PAH data (Table S5) and was fitted using the following two equations:

$$\text{One-parameter model:} \quad \Phi = A / (P_L + A) \quad (1)$$

$$\text{Two-parameter model:} \quad \Phi = 1 / (1 + 10^{-m \cdot \log(P_L/Pa) - b'}) \quad (2)$$

where P_L is the vapor pressure of the sub-cooled liquid (Pa), taken from Lei et al. (2002), and A , m , and b' are fitting parameters. Regression results of all 48 samples are listed in Table S6, and plots of observed G/P partitioning and fitting curves for the two models are presented in Fig. S5. Both models have average-correlation coefficients of 0.96 and 0.97, respectively, and their fitting curves for the same sample are very similar. The curves for level B (29.1 m) are generally shifted to the right, implying an increased contribution of particulate PAHs above the forest canopy.

In order to compare G/P partitioning at different heights, fitting parameters ($\log A$, m , and b') at two heights (A-B, A-C, A-D, B-C, B-D, and C-D) were correlated (Fig. S6). Eight data sets (out of 48, 1C, 7A, 7B, 8C, 9A, 9C, 11B, and 11C in Table S6) with extreme slopes ($m > -0.6$ and $m < -2$) were excluded (Su et al., 2006). Data points clustered close to the diagonal 1:1 lines in Fig. S6, imply a small difference in the fitting parameters between two heights. According to paired students' t-test with a two-tailed distribution, significant differences ($p < 0.01$) were observed in $\log A$ (A-B, B-D), m (A-C), and b' (A-C). This suggests that the G/P partitioning behavior above and within the canopy is indeed statistically different. As parameter A is directly related to the capacity of the particles (Pankow, 1987), the red triangles for A-B to the upper right of the diagonal line (Fig. S6a) indicate that air samples at level B have a higher fraction of intermediate PAHs on particles. This is consistent with the observation of increased Φ with decreased PAH concentrations above and within the canopy (Fig. 2). Explanations for m and b' (Fig. S6b and c) are also possible; the higher values of m and b' at level C produced shallower and rightward-shifted fitting curves, resulting in higher Φ for intermediate PAHs. This supports our assertion that canopy uptake of gaseous PAHs resulted in a change in G/P partitioning.

Pankow, J. F.: Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, Atmos. Environ., 21, 2275-2283, 1987.

Table S6. Regression parameters for the two different nonlinear models

Event	Height	Two-parameter model			One-parameter model	
		m	b'	R^2	$A \times 10^5$	R^2
1	A (44.4 m)	-0.91±0.09	-3.37±0.33	0.99	20.2±3.0	0.99
	B (29.1 m)	-1.10±0.19	-3.65±0.62	0.99	49.4±5.7	0.99
	C (16.7 m)	-0.59±0.11	-2.14±0.39	0.95	27.2±8.4	0.93
	D (1.5 m)	-0.82±0.11	-3.13±0.41	0.98	16.3±3.7	0.97
2	A (44.4 m)	-0.93±0.15	-3.71±0.60	0.97	10.2±2.9	0.97
	B (29.1 m)	-1.13±0.16	-4.42±0.63	0.98	11.7±2.9	0.98
	C (16.7 m)	-0.75±0.14	-3.03±0.58	0.95	9.4±3.3	0.94
	D (1.5 m)	-0.90±0.10	-3.50±0.39	0.98	13.1±2.6	0.98
3	A (44.4 m)	-0.75±0.10	-3.30±0.45	0.98	4.3±0.8	0.98
	B (29.1 m)	-0.75±0.15	-3.15±0.66	0.96	6.4±1.9	0.96
	C (16.7 m)	-0.70±0.12	-3.07±0.53	0.97	4.2±1.0	0.96
	D (1.5 m)	-0.80±0.14	-3.40±0.61	0.97	5.4±1.2	0.97
4	A (44.4 m)	-0.93±0.15	-3.52±0.60	0.98	15.9±3.7	0.98
	B (29.1 m)	-1.04±0.11	-3.66±0.39	0.99	29.5±5.3	0.99
	C (16.7 m)	-0.69±0.16	-2.59±0.61	0.93	20.6±7.9	0.92
	D (1.5 m)	-1.12±0.12	-4.11±0.46	0.99	21.7±3.5	0.99
5	A (44.4 m)	-0.65±0.13	-3.00±0.63	0.95	2.5±0.8	0.93
	B (29.1 m)	-0.69±0.16	-3.09±0.71	0.95	3.6±1.2	0.94
	C (16.7 m)	-0.61±0.12	-2.72±0.55	0.95	3.4±1.2	0.92
	D (1.5 m)	-0.66±0.11	-3.07±0.52	0.97	2.7±0.7	0.96
6	A (44.4 m)	-1.09±0.18	-4.04±0.70	0.97	19.8±5.3	0.97
	B (29.1 m)	-0.99±0.15	-3.61±0.57	0.97	22.7±5.9	0.97
	C (16.7 m)	-0.82±0.15	-3.17±0.62	0.96	14.5±4.1	0.96
	D (1.5 m)	-0.75±0.12	-3.08±0.49	0.98	8.3±1.8	0.97
7	A (44.4 m)	-0.60±0.09	-2.28±0.38	0.96	18.7±5.6	0.95
	B (29.1 m)	-0.50±0.06	-1.99±0.26	0.97	14.1±4.5	0.93
	C (16.7 m)	-0.63±0.13	-2.18±0.47	0.93	42.9±16.2	0.92
	D (1.5 m)	-0.65±0.09	-2.53±0.37	0.97	15.0±3.6	0.97
8	A (44.4 m)	-1.04±0.13	-4.02±0.54	0.98	13.9±2.9	0.98
	B (29.1 m)	-1.13±0.13	-4.01±0.44	0.99	26.7±4.6	0.99
	C (16.7 m)	-0.59±0.07	-2.43±0.32	0.98	6.7±2.0	0.95
	D (1.5 m)	-0.75±0.13	-3.12±0.55	0.97	7.2±1.8	0.97

Table S6. Continued

Event		Two-parameter model			One-parameter model	
		m	b'	R^2	$A \times 10^5$	R^2
9	A (44.4 m)	-0.57±0.10	-2.59±0.45	0.95	3.2±1.1	0.92
	B (29.1 m)	-0.73±0.14	-3.01±0.59	0.96	8.2±2.4	0.96
	C (16.7 m)	-0.46±0.10	-2.19±0.48	0.90	2.7±1.3	0.83
	D (1.5 m)	-0.70±0.12	-2.93±0.53	0.97	6.6±1.8	0.96
10	A (44.4 m)	-0.83±0.09	-3.20±0.38	0.99	13.1±2.4	0.99
	B (29.1 m)	-0.75±0.11	-2.80±0.40	0.98	19.0±5.1	0.97
	C (16.7 m)	-0.67±0.09	-2.43±0.35	0.97	25.7±7.6	0.96
	D (1.5 m)	-0.87±0.11	-3.39±0.45	0.99	12.2±2.1	0.98
11	A (44.4 m)	-0.74±0.16	-4.06±0.94	0.94	0.3±0.1	0.93
	B (29.1 m)	-0.58±0.11	-2.99±0.60	0.94	0.3±0.1	0.90
	C (16.7 m)	-0.60±0.14	-3.22±0.78	0.91	0.3±0.1	0.90
	D (1.5 m)	-0.61±0.12	-3.21±0.66	0.94	0.3±0.1	0.92
12	A (44.4 m)	-0.85±0.16	-3.30±0.65	0.97	13.3±3.5	0.97
	B (29.1 m)	-0.80±0.10	-2.97±0.39	0.98	18.3±4.2	0.98
	C (16.7 m)	-0.69±0.10	-2.76±0.42	0.97	10.1±2.6	0.96
	D (1.5 m)	-0.70±0.07	-3.03±0.30	0.99	4.7±0.8	0.98

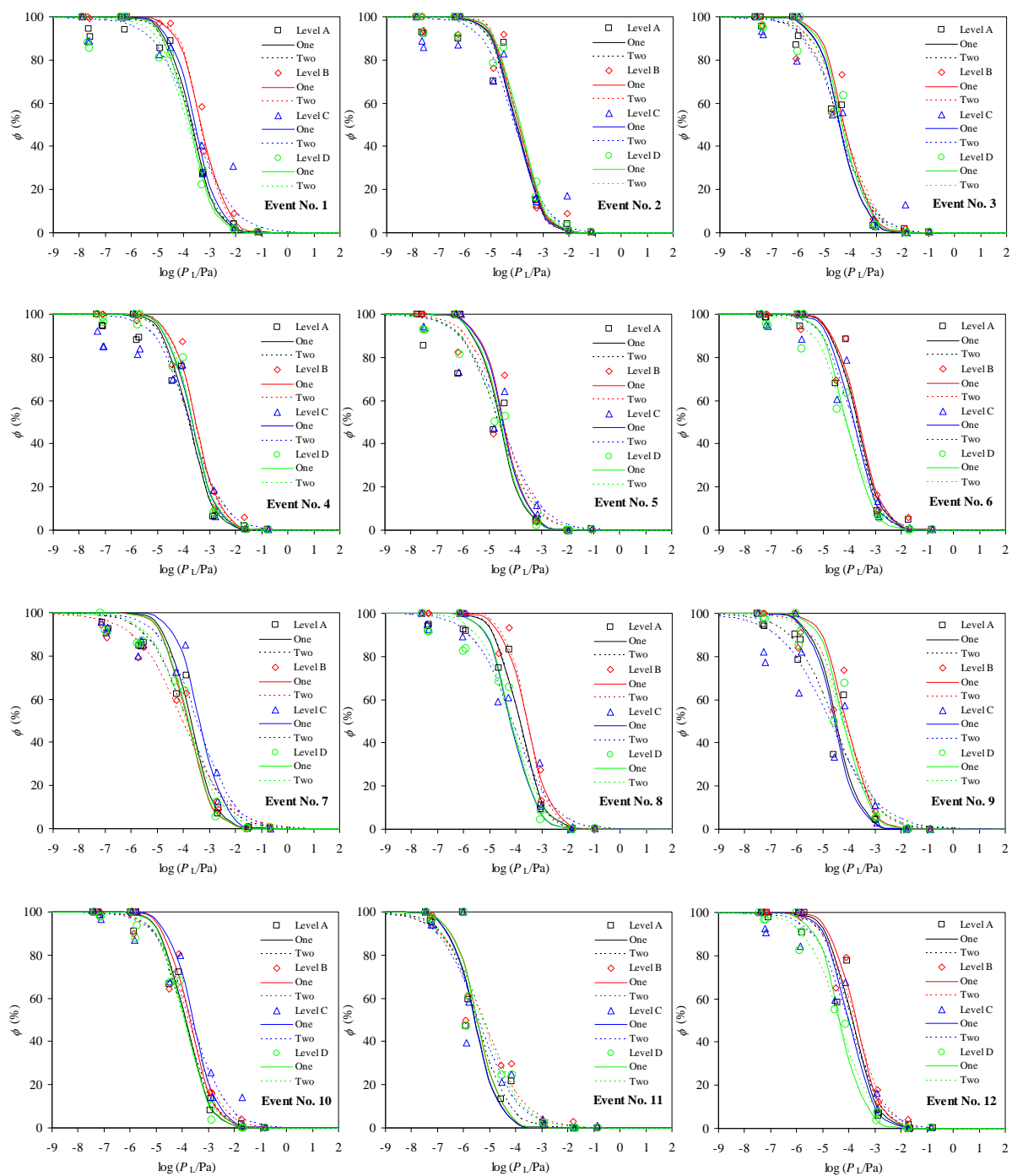


Fig. S5 Observed gas/particle partitioning behavior of 13 PAHs for all 12 sampling events and fitting curves for the nonlinear one-parameter model and nonlinear two-parameter model.

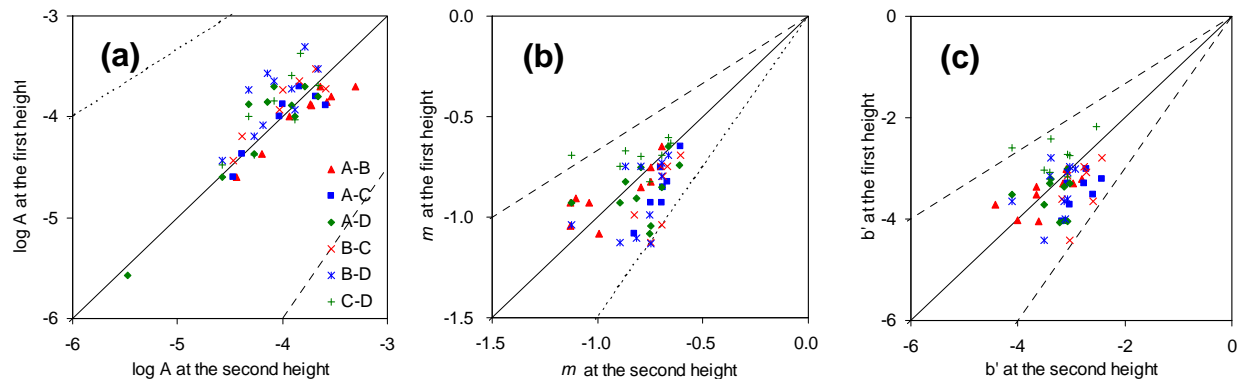


Fig. S6 Correlation plots of the fitting parameters of $\log A$ (A), m (B), and b' (C) describing the gas/particle partitioning behavior of PAHs between the different heights (A-B, A-C, A-D, B-C, B-D, and C-D). The dotted lines correspond to differences between the two heights of a factor of 1.5.

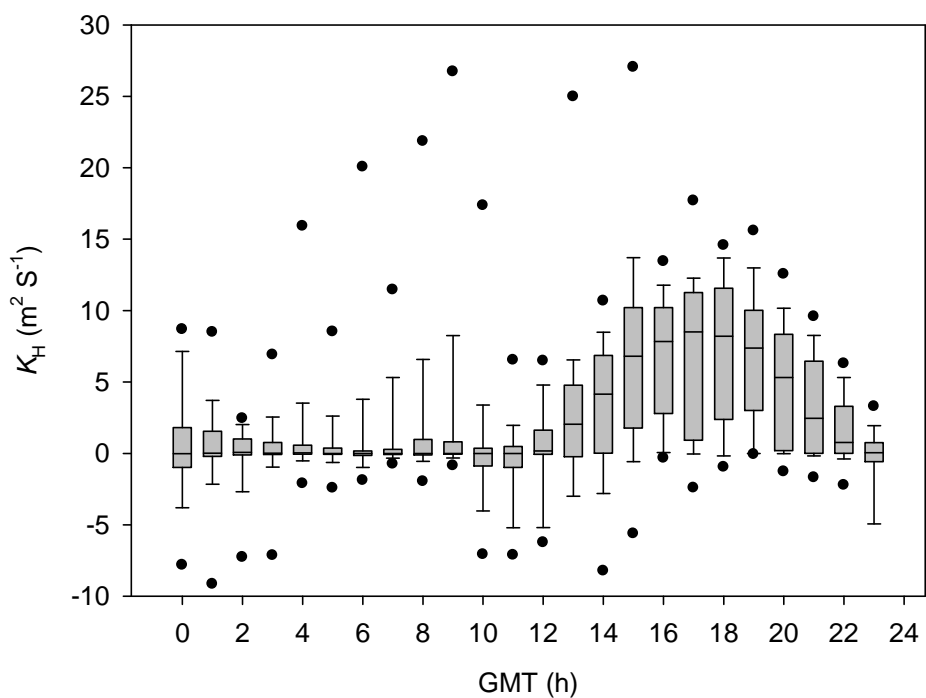


Fig. S7 Diurnal cycle of the sensible heat diffusivity (K_{Heat}) measured at Borden during the period April 20–June 10, 2003. Boxes delineate the upper and lower quartile, and the line inside the box denotes the median. Whiskers span the 10th to 90th percentile range, and circles are for 5th and 95th percentiles.

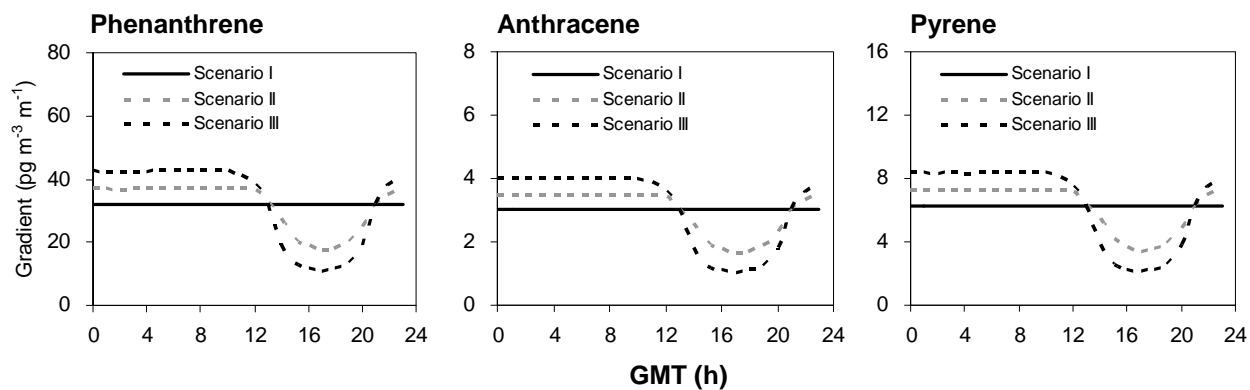


Fig. S8 Diurnal cycle of the gradient of phenanthrene, anthracene, and pyrene for three scenarios: (I) Constant gradient throughout the 24-hour sample, (II) Gradient decreasing by 50% during the day when mixing increases, while keeping the average gradient, (III) Gradient decreasing to 25%.

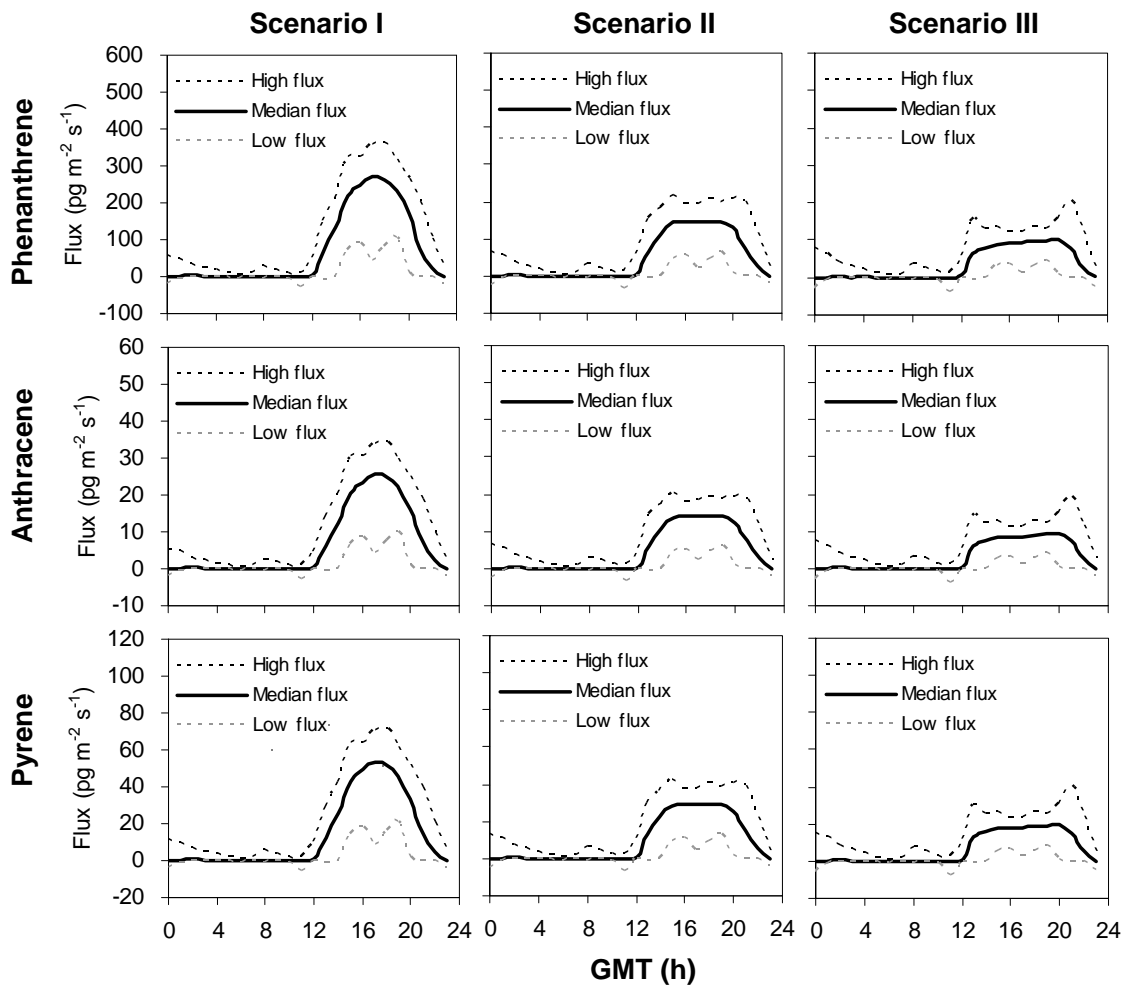


Fig. S9 Diurnal cycles of the PAH flux to the forest canopy for three different assumptions concerning the concentration gradient dC/dz : (I) Constant dC/dz throughout 24 hours, (II) dC/dz decreases by 50% during the day when mixing increases, and (III) dC/dz decreases to 25% during the day when mixing increases. High and low fluxes were calculated using upper and lower quartiles of K_{Heat} .

Table S7. Propagation of uncertainties in the input parameters to the estimates of the PAH fluxes and dry deposition velocities, based on the observed input parameter ranges. The values in gray cells exceeding the physical limit to deposition derived from the reciprocal aerodynamic resistance are considered to be unrealistic.

(a) Phenanthrene flux ($\text{pg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)

		Scenario I: $dC/dz(\text{day}) = dC/dz(\text{night})$					Scenario II: $dC/dz(\text{day}) = 0.5 \cdot dC/dz(\text{night})$					Scenario III: $dC/dz(\text{day}) = 0.25 \cdot dC/dz(\text{night})$					
		Range of K_{Heat}					Range of K_{Heat}					Range of K_{Heat}					
Range of dC/dz		Percentile	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th
Range of dC/dz	5 th		102	46	26	5	1	93	35	18	2	1	90	29	13	0	1
	25 th		219	98	57	10	3	200	75	39	4	2	194	62	28	1	2
	Median		275	124	71	13	3	251	94	48	5	3	244	77	35	1	2
	75 th		543	244	141	25	7	496	187	96	11	5	483	153	69	2	4
	95 th		663	298	172	31	8	606	228	117	13	6	589	187	84	3	5

(b) Phenanthrene deposition velocity ($\text{cm}\cdot\text{s}^{-1}$)

		Scenario I					Scenario II					Scenario III					
		Range of K_{Heat}					Range of K_{Heat}					Range of K_{Heat}					
Range of dC/dz		Percentile	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th
Range of dC/dz	5 th		10	4	3	0	0	9	3	2	0	0	9	3	1	0	0
	25 th		21	9	5	1	0	19	7	4	0	0	18	6	3	0	0
	Median		26	12	7	1	0	24	9	5	1	0	23	7	3	0	0
	75 th		51	23	13	2	1	47	18	9	1	0	46	15	7	0	0
	95 th		63	28	16	3	1	57	22	11	1	1	56	18	8	0	0

Table S7. Continued

(c) Anthracene flux ($\text{pg}\cdot\text{m}^{-2}\text{s}^{-1}$)

Scenario I						Scenario II						Scenario III											
						Range of K_{Heat}						Range of K_{Heat}						Range of K_{Heat}					
Range of dC/dz						Percentile	95 th	75 th	Median	25 th	5 th	Percentile	95 th	75 th	Median	25 th	5 th	Percentile	95 th	75 th	Median	25 th	5 th
5 th						3	1	1	0	0	3	1	1	0	0	3	1	0	0	0			
25 th						21	10	6	1	0	20	7	4	0	0	19	6	3	0	0			
Median						26	12	7	1	0	24	9	5	1	0	23	7	3	0	0			
75 th						43	20	11	2	1	40	15	8	1	0	39	12	5	0	0			
95 th						75	34	20	3	1	69	26	13	1	1	67	21	10	0	1			

(d) Anthracene deposition velocity ($\text{cm}\cdot\text{s}^{-1}$)

Scenario I						Scenario II						Scenario III											
						Range of K_{Heat}						Range of K_{Heat}						Range of K_{Heat}					
Range of dC/dz						Percentile	95 th	75 th	Median	25 th	5 th	Percentile	95 th	75 th	Median	25 th	5 th	Percentile	95 th	75 th	Median	25 th	5 th
5 th						5	2	1	0	0	5	2	1	0	0	5	2	1	0	0			
25 th						36	16	9	2	0	32	12	6	1	0	32	10	4	0	0			
Median						43	19	11	2	1	39	15	8	1	0	38	12	5	0	0			
75 th						72	32	19	3	1	66	25	13	1	1	64	20	9	0	1			
95 th						125	56	32	6	2	114	43	22	2	1	111	35	16	1	1			

Table S7. Continued

(e) Pyrene flux ($\text{pg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)

Scenario I						Scenario II						Scenario III					
Range of K_{Heat}						Range of K_{Heat}						Range of K_{Heat}					
Percentile	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th		
Range of dC/dz	5 th	25	11	6	1	0	22	8	4	0	0	22	7	3	0	0	
	25 th	49	22	13	2	1	45	17	9	1	0	44	14	6	0	0	
	Median	54	24	14	3	1	49	19	10	1	0	48	15	7	0	0	
	75 th	112	50	29	5	1	103	39	20	2	1	100	32	14	0	1	
	95 th	124	56	32	6	2	114	43	22	2	1	110	35	16	1	1	

(f) Pyrene deposition velocity ($\text{cm}\cdot\text{s}^{-1}$)

Scenario I						Scenario II						Scenario III					
Range of K_{Heat}						Range of K_{Heat}						Range of K_{Heat}					
Percentile	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th	95 th	75 th	Median	25 th	5 th		
Range of dC/dz	5 th	22	10	6	1	0	20	7	4	0	0	19	6	3	0	0	
	25 th	43	19	11	2	1	39	15	8	1	0	38	12	5	0	0	
	Median	47	21	12	2	1	43	16	8	1	0	42	13	6	0	0	
	75 th	98	44	26	5	1	90	34	17	2	1	87	28	12	0	1	
	95 th	109	49	28	5	1	100	37	19	2	1	97	31	14	0	1	