

Supporting Information for:
**Annual Variations of PAH Concentrations in Precipitation
 Collected Near the Great Lakes.**

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This supporting Information contains seven tables of values derived from modeled parameters for PAHs at seven IADN sites. ΣPAH is the sum of 14 PAHs measured by both Indiana University and National Laboratory for Environmental Testing (NLET) in Burlington. These PAH are fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, triphenylene + chrysene (count as one compound), benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]-pyrene, benzo[a]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[ghi]perylene, and dibenz[a,h]-anthracene.

The following equation was used to fit the data:

$$\ln C_p = a_0 + a_1 t + a_2 \sin\left(\frac{t}{a_3} + a_4\right)$$

where t is the time in Julian Days relative to January 1 1990, a_0 is the intercept (unitless), a_1 is a first-order rate constant (in days⁻¹) describing the rate of exponential decrease or increase over time, a_2 is the periodic amplitude (unitless), a_3 is the length of the period (in days), and a_4 is the periodic offset (in days).

Because 74 of the 105 datasets had a period length (a_3) of 368 ± 12 days, the period length for all 105 of these datasets was forced to be one year, which simplified the calculation of the date during the year when the PAH concentrations reached their maximum.

The tables show results of the fit to this sinusoidal model with a_3 of 365 days. The results are listed as mean \pm standard error. Normal font numbers are significant for $0.01 < P < 0.05$; italic font numbers are significant for $0.001 < P < 0.01$, bold font numbers are significant at level of $P < 0.001$. “NS” means “not significant at $P > 0.05$. A negative half-life is actually a doubling time.

Table S1. Fit parameters for PAHs at Brule River

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio _O , e^{2a_2}	Maximum date (\pm days)	No. of detectors	Average conc. (ng/L)	R^2
Fluorene	-6.3 \pm 2.1*	3.1 \pm 1.2	Feb 11 \pm 10	63	1.0 \pm 0.1	0.37
Phenanthrene	NS	2.8 \pm 1.2	<i>Feb 14 \pm 12</i>	64	5.7 \pm 0.5	0.29
Anthracene	Limited data	NS	Feb 13 \pm 7	23	0.3 \pm 0.1	
Fluoranthene	NS	5.8 \pm 1.3	Feb 8 \pm 9	64	5.3 \pm 0.9	0.51
Pyrene	NS	5.6 \pm 1.3	Jan 21 \pm 15	59	3.3 \pm 0.5	0.42
Retene	-5.1 \pm 2.4*	3.0 \pm 1.4	NS	63	2.0 \pm 0.3	0.21
Benz[a]anthracene	NS	NS	NS	46	0.9 \pm 0.2	NS
Triphenylene + chrysene	NS	7.7 \pm 1.3	Feb 7 \pm 6	64	2.3 \pm 0.3	0.58
Benzo[b]fluoranthene	NS	9.3 \pm 1.3	Feb 7 \pm 6	63	3.3 \pm 0.6	0.60
Benzo[k]fluoranthene	NS	4.8 \pm 1.4	Feb 3 \pm 10	40	1.2 \pm 0.1	0.40
Benzo[e]pyrene	NS	6.5 \pm 1.3	Feb 7 \pm 7	58	1.6 \pm 0.2	0.50
Benzo[a]pyrene	NS	7.0 \pm 1.4	Feb 7 \pm 8	50	1.7 \pm 0.4	0.48
Indeno[1,2,3-cd]pyrene	NS	7.4 \pm 1.3	Feb 5 \pm 7	57	2.3 \pm 0.5	0.52
Benzo[ghi]perylene	NS	6.7 \pm 1.3	Feb 6 \pm 7	58	1.9 \pm 0.3	0.52
Dibenz[a,h]anthracene	Limited data	NS	NS	10	0.3 \pm 0.1	
Coronene	NS	8.0 \pm 1.4	Jan 31 \pm 8	35	1.2 \pm 0.2	0.53
ΣPAH	NS	5.3 \pm 1.2	Feb 8 \pm 7	64	29 \pm 4.3	0.39

*A negative half-life indicates that the concentrations are increasing and the listed value is the doubling time.

Table S2. Fit parameters for PAHs at Eagle Harbor

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (± days)	No. of detects	Average conc. (ng/L)	R^2
Fluorene	NS	3.3 ± 1.2	Jan 30 ± 8	80	0.8 ± 0.1	0.38
Phenanthrene	NS	3.5 ± 1.2	Jan 31 ± 8	82	4.7 ± 0.4	0.35
Anthracene	Limited data	NS	5.6 ± 1.2	20	0.3 ± 0.1	
Fluoranthene	NS	5.1 ± 1.2	Feb 4 ± 6	82	5.1 ± 0.5	0.51
Pyrene	NS	4.3 ± 1.3	Feb 3 ± 8	77	3.0 ± 0.3	0.43
Retene	-5.4 ± 2.0*	NS	Dec 28 ± 11	82	2.0 ± 0.3	0.33
Benz[a]anthracene	NS	5.9 ± 1.3	Jan 24 ± 7	61	0.9 ± 0.1	0.50
Triphenylene + chrysene	NS	6.0 ± 1.2	Jan 24 ± 6	82	2.2 ± 0.2	0.50
Benzo[b]fluoranthene	NS	6.4 ± 1.2	Jan 29 ± 6	79	3.1 ± 0.3	0.55
Benzo[k]fluoranthene	NS	3.8 ± 1.3	Jan 20 ± 10	50	1.4 ± 0.1	0.39
Benzo[e]pyrene	NS	4.2 ± 1.2	Jan 26 ± 8	72	1.6 ± 0.1	0.39
Benzo[a]pyrene	NS	3.3 ± 1.3	Jan 21 ± 11	65	1.4 ± 0.1	0.31
Indeno[1,2,3-cd]pyrene	NS	6.4 ± 1.2	Jan 30 ± 6	74	2.3 ± 2.6	0.54
Benzo[ghi]perylene	NS	4.9 ± 1.2	Jan 30 ± 7	76	1.8 ± 0.2	0.49
Dibenz[a,h]anthracene	Limited data	NS		6	0.3 ± 0.1	
Coronene	NS	5.5 ± 1.3	Jan 23 ± 9	39	1.1 ± 0.1	0.54
ΣPAH	NS	5.4 ± 1.2	Jan 27 ± 6	82	26 ± 2.5	0.51

*A negative half-life indicates that the concentrations are increasing and the listed value is the doubling time.

Table S3. Fit parameters for PAHs at Sleeping Bear Dunes

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (± days)	No. of detects	Average conc. (ng/L)	R^2
Fluorene	NS	3.4 ± 1.2	Feb 11 ± 8	80	1.3 ± 0.1	0.39
Phenanthrene	NS	4.9 ± 1.3	Feb 17 ± 8	82	6.3 ± 0.6	0.38
Anthracene	NS	4.6 ± 1.5	Feb 3 ± 7	45	0.3 ± 0.0	0.52
Fluoranthene	NS	5.6 ± 1.2	Feb 20 ± 7	83	8.1 ± 0.7	0.46
Pyrene	NS	5.3 ± 1.2	Feb 11 ± 6	81	4.6 ± 0.4	0.55
Retene	-9.5 ± 4.7*	3.9 ± 1.2	Feb 1 ± 7	82	1.3 ± 0.1	0.46
Benz[a]anthracene	NS	4.9 ± 1.2	Feb 5 ± 6	76	1.6 ± 0.1	0.59
Triphenylene + chrysene	NS	4.0 ± 1.2	Feb 5 ± 5	83	3.5 ± 0.3	0.64
Benzo[b]fluoranthene	NS	6.0 ± 1.2	Feb 5 ± 5	83	5.3 ± 0.5	0.68
Benzo[k]fluoranthene	NS	4.5 ± 1.2	Feb 6 ± 7	73	1.9 ± 0.2	0.53
Benzo[e]pyrene	NS	4.9 ± 1.2	Feb 5 ± 5	80	2.5 ± 0.2	0.58
Benzo[a]pyrene	NS	4.4 ± 1.2	Feb 4 ± 6	80	2.3 ± 0.2	0.54
Indeno[1,2,3-cd]pyrene	NS	5.1 ± 1.2	Feb 1 ± 5	80	3.6 ± 0.3	0.61
Benzo[ghi]perylene	NS	4.7 ± 1.1	Jan 31 ± 5	81	3.0 ± 0.2	0.62
Dibenz[a,h]anthracene	Limited data			29	0.5 ± 0.1	
Coronene	8.2 ± 2.8	5.2 ± 1.2	Jan 30 ± 6	65	1.5 ± 0.1	0.64
ΣPAH	NS	5.3 ± 1.2	Feb 5 ± 5	83	43 ± 3.5	0.64

*A negative half-life indicates that the concentrations are increasing and the listed value is the doubling time.

Table S4. Fit parameters for PAHs at Surgeon Point

PAHs	Half-life (years) $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (\pm days)	No. of detects	Average Conc. (ng/L)	R^2
Fluorene	NS	2.6 ± 1.1	Feb 18 ± 7	85	2.3 ± 1.4	0.43
Phenanthrene	NS	3.6 ± 1.2	Feb 20 ± 7	85	13 ± 1.0	0.45
Anthracene	NS	4.3 ± 1.3	Feb 10 ± 7	73	0.7 ± 0.1	0.47
Fluoranthene	NS	4.0 ± 1.2	Feb 12 ± 7	85	19 ± 1.5	0.45
Pyrene	NS	4.0 ± 1.2	Feb 13 ± 8	85	9.4 ± 0.8	0.39
Retene	NS	3.2 ± 1.2	Feb 1 ± 9	83	1.3 ± 0.1	0.34
Benz[a]anthracene	NS	4.0 ± 1.2	Feb 16 ± 7	81	3.4 ± 0.3	0.47
Triphenylene + chrysene	NS	4.0 ± 1.2	Feb 6 ± 8	85	6.8 ± 0.6	0.43
Benzo[<i>b</i>]fluoranthene	NS	3.6 ± 1.2	Feb 11 ± 8	85	10 ± 0.9	0.36
Benzo[<i>k</i>]fluoranthene	NS	3.2 ± 1.2	Feb 14 ± 8	82	3.5 ± 0.3	0.37
Benzo[<i>e</i>]pyrene	NS	3.6 ± 1.2	Feb 13 ± 7	84	4.5 ± 0.3	0.41
Benzo[<i>a</i>]pyrene	NS	3.3 ± 1.2	Feb 14 ± 8	84	4.6 ± 0.4	0.35
Indeno[1,2,3- <i>cdf</i>]pyrene	NS	3.2 ± 1.2	Feb 8 ± 10	84	6.7 ± 0.6	0.30
Benzo[<i>gh</i>]perylene	NS	3.5 ± 1.2	Feb 8 ± 8	83	5.3 ± 0.4	0.40
Dibenz[<i>a,h</i>]anthracene	NS	2.4 ± 1.2	Feb 24 ± 11	65	1.0 ± 0.1	0.27
Coronene	NS	3.8 ± 1.2	Jan 31 ± 7	81	2.0 ± 0.2	0.46
ΣPAH	NS	3.5 ± 1.2	Feb 10 ± 8	85	90 ± 6.9	0.40

Table S5. Fit parameters for PAHs at Chicago

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (\pm days)	No. of detects	Average conc. (ng/L)	R^2
Fluorene	3.4 ± 0.8	2.0 ± 1.3	NS	70	36 ± 8.6	0.29
Phenanthrene	3.0 ± 0.7	2.4 ± 1.4	NS	70	290 ± 72	0.45
Anthracene	2.0 ± 0.4	4.0 ± 1.7	NS	70	34 ± 8.3	0.38
Fluoranthene	2.9 ± 0.7	3.9 ± 1.1	Mar 4 ± 3	70	480 ± 130	0.49
Pyrene	2.7 ± 0.6	4.2 ± 1.4	NS	70	290 ± 82	0.37
Retene	4.7 ± 2.3	4.8 ± 1.3	Mar 7 ± 12	69	7.3 ± 1.7	0.35
Benz[a]anthracene	2.3 ± 0.5	5.4 ± 1.5	NS	70	140 ± 41	0.41
Triphenylene + chrysene	2.3 ± 0.5	5.1 ± 1.4	Mar 1 ± 13	70	160 ± 46	0.44
Benzo[b]fluoranthene	3.0 ± 0.8	3.6 ± 1.2	Mar 5 ± 14	70	230 ± 63	0.37
Benzo[k]fluoranthene	2.4 ± 0.5	5.1 ± 1.4	Mar 1 ± 13	70	79 ± 22	0.42
Benzo[e]pyrene	2.8 ± 0.7	4.9 ± 1.4	Mar 3 ± 13	70	93 ± 27	0.38
Benzo[a]pyrene	2.4 ± 0.6	4.9 ± 1.5	NS	70	170 ± 51	0.37
Indeno[1,2,3-cd]pyrene	3.1 ± 0.9	4.6 ± 1.4	NS	70	150 ± 40	0.33
Benzo[ghi]perylene	3.1 ± 0.9	4.4 ± 1.4	Mar 3 ± 14	70	100 ± 27	0.34
Dibenz[a,h]anthracene	2.6 ± 0.7	4.9 ± 1.5	NS	69	28 ± 8.2	0.36
Coronene	2.7 ± 0.6	3.8 ± 1.4	Feb 25 ± 16	70	26 ± 7.2	0.35
ΣPAH	2.8 ± 0.6	3.8 ± 1.4	NS	70	2300 ± 620	0.38

Table S6. Fit parameters for PAHs at Burnt Island

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (\pm days)	No. of detected	Average conc. (ng/L)	R^2
Fluorene	4.7 ± 1.2	4.7 ± 1.3	Jan 23 ± 10	76	2.2 ± 0.3	0.38
Phenanthrene	3.8 ± 0.8	5.5 ± 1.3	Jan 18 ± 8	79	16 ± 2.3	0.43
Anthracene	Limited data			20	2.0 ± 0.9	
Fluoranthene	6.3 ± 2.1	7.8 ± 1.2	Jan 17 ± 6	79	13 ± 1.4	0.58
Pyrene	6.3 ± 2.1	6.4 ± 1.3	Jan 19 ± 7	80	8.0 ± 1.0	0.47
Retene	Not available					
Benz[a]anthracene	NS	4.6 ± 1.4	Jan 2 ± 12	39	1.6 ± 0.3	0.44
Chrysene	NS	6.2 ± 1.3	Jan 10 ± 9	39	4.8 ± 0.8	0.53
Benzo[b]fluoranthene	NS	7.9 ± 1.4	Jan 23 ± 9	64	6.7 ± 0.9	0.38
Benzo[k]fluoranthene	NS	7.8 ± 1.4	Jan 16 ± 9	62	4.4 ± 0.6	0.41
Benzo[e]pyrene	NS	6.3 ± 1.4	Jan 4 ± 10	34	3.2 ± 0.6	0.56
Benzo[a]pyrene	NS	3.3 ± 1.4	Jan 10 ± 14	52	1.7 ± 0.4	0.48
Indeno[1,2,3-cd]pyrene	NS	7.5 ± 1.4	Jan 25 ± 8	57	3.8 ± 0.5	0.40
Benzo[ghi]perylene	NS	5.1 ± 1.4	Jan 11 ± 11	59	3.9 ± 0.5	0.34
Dibenz[a,h]anthracene	Limited data			16	0.8 ± 0.1	
Perylene	Limited data			16	0.8 ± 0.1	
Coronene	Not available					
ΣPAH	NS	7.0 ± 1.3	Jan 23 ± 7	80	60 ± 7.2	0.46

Table S7. Fit parameters for PAHs at Point Petre

PAHs	Half-life (years), $(\ln 2)/365^*a_1$	Peak-to-valley ratio, e^{2a_2}	Maximum date (± days)	No. of detects	Average conc. (ng/L)	R^2
Fluorene	6.3 ± 2.1	4.0 ± 1.2	Jan 23 ± 8	72	2.3 ± 0.3	0.43
Phenanthrene	4.7 ± 1.1	4.6 ± 1.2	Jan 23 ± 7	81	17 ± 2.3	0.49
Anthracene	Limited data					
Fluoranthene	6.3 ± 1.7	5.5 ± 1.2	Jan 23 ± 6	18	1.9 ± 0.8	
Pyrene	4.7 ± 1.0	4.6 ± 1.2	Jan 13 ± 7	80	18 ± 2.2	0.60
Retene	Not available					
Benz[a]anthracene	NS	4.0 ± 1.4	Jan 11 ± 12	38	2.2 ± 0.3	0.42
Chrysene	NS	4.2 ± 1.4	Jan 18 ± 12	38	7.5 ± 1.0	0.38
Benzo[b]fluoranthene	NS	7.2 ± 1.3	Jan 10 ± 7	55	10 ± 1.5	0.52
Benzo[k]fluoranthene	NS	9.0 ± 1.3	Jan 13 ± 7	54	5.9 ± 0.8	0.56
Benzo[e]pyrene	NS	4.6 ± 1.4	Jan 18 ± 11	37	4.9 ± 0.6	0.46
Benzo[a]pyrene	NS	4.5 ± 1.4	Jan 12 ± 11	59	3.1 ± 0.3	0.28
Indeno[1,2,3-cd]pyrene	NS	4.7 ± 1.3	Jan 24 ± 8	69	4.6 ± 0.4	0.41
Benzo[ghi]perylene	NS	4.3 ± 1.3	Jan 26 ± 9	61	4.4 ± 0.4	0.36
Dibenz[a,h]anthracene	Limited data					
Perylene	Limited data					
Coronene	Not available					
ΣPAH	NS	6.2 ± 1.2	Jan 22 ± 6	81	76 ± 8.0	0.55