SUPPORTING INFORMATION

Century-long source apportionment of PAHs in Athabasca oil sands region lakes using diagnostic ratios and compound-specific carbon isotope signatures

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Text S1. Analysis and quantification of PAHs

The following PAH standards were used: coronene, perylene, dibenzothiophene and retene (Sigma-Aldrich); 16 EPA Priority PAH mixture, 2-methylanthracene, 9,10-dimethylanthracene, 1-methylnaphthalene, 1,4-dimethylnaphthalene, 1-methylphenanthrene and 1-methylfluorene (Anachemia Science).

The limits of quantification are the lowest concentration on the calibration curve converted into ng of PAHs per gram of sediment (dry weight). As the weight of sediment extracted depended on the amount of material available in each layer of the core, we are reporting here a lowest quantification limit and a highest quantification limit (based on a 11.3 g and 3.1 g sediment extraction). The limits of quantification were between 0.22 ng g^{-1} to 0.80 ng g^{-1} for ALE and 0.12 ng g^{-1} to 0.50 ng g^{-1} for ALD. PAH concentrations below the limits of quantification are not reported.

Limits of detection were estimated as 3 times the height of the baseline for an analyte peak on a chromatogram. As GC-MS analysis was carried out using Single Ion Monitoring (SIM) mode, our baseline was relatively variable across the entire chromatogram inducing LoD for some PAHs higher than their LoQ. We are not reporting any concentrations under this high LoD for these PAHs.

Text S2. Individual PAH concentrations

Perylene concentrations (Tables S1 & S2) in both lakes showed a down-core increase. This pattern is typically associated with sediment diagenesis.[1, 2]

Retene concentrations (Table S1 & S2) are comparable in both lakes with a baseline concentration around 50 ng g^{-1}. An increase in concentration at the top of the ALE core is attributed to early diagenetic processes[1] since no evidence of proximal forest fire activity has been reported in the last decade.[3] A peak of retene in ALD at 18 cm depth (dated 1934) may be related to an input of terrestrial material, since there was no evidence for an associated increase in pyrogenic PAHs in this layer (Table S2). In addition, sediment mixing in ALD may have an averaging effect on the sediment record of retene concentrations.

DBT and C1-C4 DBTs are present at lower relative concentrations in our cores (0.5-2.9% for ALD and 0.01-0.24% for ALE) compared to the 3 lakes east of the operations reported by Kurek et al.[4] (3-17%). However, concentrations of DBTs in Athabasca oil sands are variable,[5] and as our study sites are situated at least two times further east, this discrepancy illustrates the relationship between atmospheric transport with distance to the source.

Table S1. Concentrations of the target PAHs in ng g^{-1} of dried sediment (corrected for recovery) and sediment accumulation rate derived from the CRS model for ALE. The error is the average standard deviation of duplicate extractions of sediment sub-sampled from the same depth interval (n = 3 different depth intervals). With $\sum PAH_{parent}$, the sum of the 16 EPA PAHs minus naphthalene, $\sum PAH_{alkyl}$ the sum of the alkylated PAH groups (C1-C4 phenanthrene/anthracene, C1-C4 fluoranthene/pyrene, C1-C4 dibenzothiophene (DBT), C1-C4 fluorene, C1-C4 chrysene) and $\sum PAH_{total}$ the sum of $\sum PAH_{parent}$ and $\sum PAH_{alkyl}$.

PAH (sediment layer, cm)	*0-1*	*1-2*	*2-3*	*3-4*	*4-5*	*5-6*	*6-7*	*7-8*	*8-9*	*9-10*	*10-11*	*12-13*	*13-14*	*14-15*	*15-16*	*16-17*	*17-18*	*18-19*	*19-20*	*20-21*	*21-22*	*22-23*	*LoQ max*	*LoQ min*	*LoD max*	*LoD min*	*Error (ng.g^{-1})*
Naphthalene	4.92	2.86	2.99	3.36	0.54	0.84			11.78	24.24	5.84	16.70	10.58	15.42	0.48			9.02	9.41	11.55	61.95	50.97	0.22	0.81	0.09	0.32	12.90
C1- Naphthalene	12.29	10.97	8.14	11.73	3.76	5.13	0.62	0.29	27.01	32.42	19.87	24.39	17.80	22.54	5.05	2.06		22.89	17.34	25.05	66.85	51.66	0.22	0.81	0.09	0.32	11.00
C2- Naphthalene	8.28	8.52	7.63	9.01	5.57	5.20	2.38	1.76	12.71	12.41	12.82	11.56	10.32	10.64	6.52	5.34	0.88	10.96	8.62	10.88	16.97	14.30	0.22	0.81	0.11	0.39	0.91
C3- Naphthalene	50.38	48.65	45.88	47.60	40.53	34.35	29.43	24.55	43.65	44.58	49.34	47.07	45.55	46.65	38.31	33.01	22.68	46.08	34.48	40.47	58.36	50.54	0.22	0.81	0.11	0.39	1.39
C4- Naphthalene																							0.22	0.81			
Acenaphthylene			0.62			0.78			1.45	1.05	0.79	1.36	1.21	0.93	1.21		0.69	1.30	0.78	0.91	1.84	1.60	0.22	0.81	0.17	0.61	0.19
Acenaphthene	3.50	3.56	3.58	4.82	3.53	3.96	3.10	1.99	6.63	5.62	6.80	6.77	6.50	8.04	6.05	4.46	1.57	7.18	5.81	6.94	10.31	9.63	0.22	0.81	0.14	0.52	0.36
Fluorene	11.32	10.39	11.69	13.29	9.94	10.16	9.02	8.93	15.94	14.96	17.27	16.54	19.58	22.26	24.01	20.16	14.08	21.43	20.95	19.61	26.10	24.23	0.22	0.81	0.19	0.68	0.48
C1-Fluorene	7.72	7.20	6.28	3.71	5.23	5.75	4.66	4.50	6.12	9.73	8.38	6.73	6.72	7.30	6.71	5.99	7.36	6.65	6.03	8.00	7.95	7.64	0.22	0.81	0.19	0.68	0.05
C2-Fluorene																											
C3-Fluorene	18.91	17.93	16.23	9.52	9.44	14.38	14.80	9.34	8.76	12.17	11.50	13.05	9.08	10.74	9.75	8.63	12.06	12.29	9.15	12.74	14.79	11.64	0.22	0.81	0.19	0.68	0.27
C4-Fluorene																											
Dibenzothiophene	1.37	0.99	1.43	1.44	1.05	0.75	0.78	0.57	0.77	0.69	0.82	0.75	0.72	1.03	0.74	0.85	0.94	0.86	0.75	1.18	1.00	0.93	0.22	0.81	0.14	0.52	0.07
C1-Dibenzothiophene																							0.22	0.81			
C2-Dibenzothiophene																							0.22	0.81			
C3-Dibenzothiophene																											
C4-Dibenzothiophene																							0.22	0.81			
Phenanthrene	40.27	35.40	37.33	34.99	35.64	32.93	35.08	28.07	36.03	36.34	36.74	47.92	38.85	45.24	47.07	37.51	39.56	46.56	38.87	41.07	59.79	46.04	0.22	0.81	0.20	0.71	0.73
Anthracene	5.79	5.40	4.74	2.89	3.50	3.15	3.91	6.76	5.96	9.12	7.69	13.23	10.50	12.67	11.91	11.39	7.78	13.15	11.81	12.58	15.86	13.50	0.22	0.81	0.20	0.71	0.43
C1-Phen/Anth	28.76	29.28	33.58	27.83	32.97	25.58	25.46	24.99	23.41	20.64	28.49	44.13	28.19	34.71	29.99	28.70	29.21	42.86	31.75	33.66	44.59	33.21	0.22	0.81	0.20	0.71	0.72
C2-Phen/Anth	16.39	21.40	16.60	19.12	8.21	16.97	16.02	6.48	12.91	11.16	17.64	17.25	13.89	19.18	14.34	15.31	8.12	22.54	17.53	19.80	27.53	18.30	0.22	0.81	0.65	2.35	0.15
C3-Phen/Anth																							0.22	0.81			

C4-Phen/Anth																							0.22	0.81			
Fluoranthene	14.74	13.47	13.60	15.94	14.88	13.82	14.71	14.60	20.26	21.65	19.84	22.13	15.38	24.31	28.81	20.32	22.08	24.76	18.04	19.52	43.79	23.35	0.22	0.81	0.57	2.06	0.43
Pyrene	46.54	45.22	43.23	41.45	40.57	30.73	36.87	32.94	64.77	57.21	55.13	67.75	42.39	68.30	83.26	40.81	23.86	74.02	29.77	33.35	90.73	58.10	0.22	0.81	0.49	1.77	1.05
C1-Fluoth/Py	9.70	10.56	11.78	8.68	11.61	9.76	10.53	9.09	9.62	8.49	9.30	13.79	10.20	13.15	13.09	14.18	15.96	15.05	14.00	14.69	15.66	14.06	0.22	0.81	0.53	1.91	0.41
C2-Fluoth/Py																							0.22	0.81			
C3-Fluoth/Py																							0.22	0.81			
C4-Fluoth/Py																							0.22	0.81			
Retene	116.24	213.34	84.35	45.27	75.41	67.24	60.70	38.64	35.67	39.23	43.55	44.81	40.54	49.82	42.68	41.09	46.27	54.44	39.89	38.42	56.40	46.10	0.22	0.81	0.63	2.26	2.45
Benzo[a]anthracene	7.72	8.66	8.46	9.15	8.07	6.65	8.33	5.16	5.00	5.00	7.89	5.26	4.13	5.69	4.99	5.25	7.45	8.61	6.94	8.61	8.73	8.17	0.22	0.81	0.15	0.55	0.76
Chrysene	10.35	11.34	11.45	10.31	9.35	8.32	7.93	5.90	5.76	5.21	6.02	6.18	4.73	5.66	5.94	6.13	7.76	5.92	5.70	7.07	7.74	6.65	0.22	0.81	0.15	0.55	0.34
C1-Chrysene	35.72	29.96	28.85	33.85	26.23	23.56	23.10	20.11	19.06	28.26	20.14	14.03	11.87	14.15	13.85	13.74	20.96	16.49	15.30	20.43	17.95	16.81	0.22	0.81	0.15	0.55	0.48
C2-Chrysene																							0.22	0.81			
C3-Chrysene																							0.22	0.81			
C4-Chrysene																											
Benzo[b]fluoranthene	19.54	18.35	19.57	22.64	21.13	15.90	16.52	12.62	17.70	19.29	18.35	15.65	12.85	15.21	14.48	16.28	25.69	17.86	16.95	21.37	18.72	17.20	0.22	0.81	0.13	0.45	0.34
Benzo[k]fluoranthene	1.20	1.30	1.67	1.43	1.37	1.58	1.73	1.75	2.27	1.24	1.92	1.94	2.20	2.75	2.09	2.14	2.49	1.87	1.97	1.31	1.84	0.77	0.22	0.81	0.14	0.52	0.20
Benzo[a]pyrene	9.94	9.93	9.70	10.00	9.09	8.51	9.19	8.22	7.50	8.05	8.92	7.15	6.06	7.37	7.75	8.12	11.73	8.36	8.15	9.69	9.09	8.41	0.22	0.81	0.17	0.61	0.60
Perylene	89.43	91.96	116.45	155.09	122.15	196.05	231.83	219.19	259.20	271.96	270.00	270.41	261.17	349.62	395.35	434.13	510.54	492.45	504.93	522.13	526.26	468.47	0.22	0.81	0.31	1.13	8.06
Indeno[1,2,3-cd]pyrene	8.01	8.65	9.07	11.30	10.30	10.75	10.85	11.19	11.02	13.74	12.46	10.48	8.80	10.73	10.90	11.51	18.46	12.25	11.40	13.92	12.42	11.16	0.22	0.81	0.16	0.58	0.21
Dibenzo[a,h]anthracene	2.45	2.89	3.18	3.10	3.57	2.21	2.45	2.05	2.37	2.34	2.34	2.20	1.83	2.30	2.31	3.02	2.52	3.22	3.11	0.00	1.55		0.22	0.81	0.17	0.61	0.73
Benzo[g,h,i]perylene	16.56	16.14	16.12	18.24	15.25	15.06	14.86	14.63	14.08	17.70	15.47	13.33	11.25	13.62	14.03	14.53	22.72	15.48	14.36	16.73	14.78	13.45	0.22	0.81	0.18	0.65	0.23
Coronene	7.30	5.04	8.38	9.48	9.62	10.08	10.74	10.51	10.36	12.16	11.37	10.17	8.56	10.72	11.08	11.52	16.74	11.99	11.18	11.41	10.28	9.10	0.22	0.81	0.44	1.58	0.20
$\sum PAH_{total}$	316.50	308.02	308.76	303.70	280.93	261.26	269.90	229.89	297.39	309.66	313.90	347.62	266.93	345.34	353.28	289.03	303.05	378.71	289.12	323.18	452.75	344.85					
$\sum PAH_{parent}$	199.3	191.69	195.44	200.99	187.24	165.26	175.33	155.38	217.51	219.21	218.45	238.64	186.98	246.11	265.55	202.48	209.38	262.83	195.36	213.86	324.28	243.19					
$\sum PAH_{alkyl}$	117.2	116.33	113.32	102.71	93.69	96.00	94.57	74.51	79.88	90.45	95.45	108.98	79.95	99.23	87.73	86.55	93.67	115.88	93.76	109.32	128.47	101.66					
Mass of sediment extracted (g)	3.75	4.8	5.6	6.57	5.66	5.57	6.7	7.12	7.28	3.104	5.85	8.37	9.27	10.14	10.75	11.2	5.02	9.32	10.58	5.46	7.14	7.48					
Sediment accumulation rate ($g.m^{-2}.yr$)	130	119	113	100	102	94	93	115	121	124	118	124	133	136	130	152	135	116	107	94	105	100					

Table S2. Concentrations of the target PAHs in ng g^{-1} of dried sediment corrected for recovery for ALD. The error is the average standard deviation of duplicate extractions of sediment sub-sampled from the same depth interval (n = 3 different depth intervals). With $\sum PAH_{parent}$, the sum of the 16 EPA PAHs minus naphthalene, $\sum PAH_{alkyl}$ the sum of the alkylated PAH groups (C1-C4 phenanthrene/anthracene, C1-C4 fluoranthene/pyrene, C1-C4 dibenzothiophene (DBT), C1-C4 fluorene, C1-C4 chrysene) and $\sum PAH_{total}$ the sum of $\sum PAH_{parent}$ and $\sum PAH_{alkyl}$.

PAH (sediment layer, cm)	*0-1*	*1-2*	*2-3*	*3-4*	*4-5*	*5-6*	*6-7*	*7-8*	*8-9*	*9-10*	*10-11*	*11-12*	*12-13*	*13-14*	*14-15*	*15-16*	*16-17*	*17-18*	*18-19*	*19-20*	*20-21*	*21-22*	*22-23*	*LoQ max*	*LoQ min*	*LoD max*	*LoD min*	*Error (ng.g-1)*
Naphthalene	0.32	4.38	13.18	33.50	4.76	9.12	0.82	9.95	14.46	9.40	16.93	27.76	34.57	6.88	6.93	5.41	10.42	3.60	7.12	14.07	19.50	20.42	13.57	0.12	0.50	0.06	0.25	12.90
C1- Naphtalene	21.42	23.01	30.26	60.90	24.26	36.12	23.40	28.04	39.25	26.83	37.22	51.12	48.18	22.97	23.73	17.24	24.07	15.38	16.00	26.23	36.37	31.33	24.52	0.12	0.50	0.06	0.25	11.00
C2- Naphthalene	30.07	20.18	21.93	27.22	17.07	21.61	28.72	18.05	24.04	18.65	21.25	22.67	20.44	15.59	18.09	13.83	15.04	13.66	12.20	13.97	13.78	14.06	13.24	0.12	0.50	0.06	0.25	0.91
C3- Naphthalene	28.11	35.86	28.29	61.74	41.10	51.05	27.04	43.23	60.57	40.60	49.95	52.63	50.39	38.91	52.01	32.46	27.14	27.41	23.69	29.63	50.30	40.90	34.65	0.12	0.50	0.06	0.25	1.39
C4- Naphthalene	14.48	19.90	3.05	7.99	4.67	10.43	4.06	13.74	5.00	7.38	4.58	5.10	9.19	4.87	7.06	8.36	4.15	3.31	3.90	4.36	8.29	4.36	4.36	0.12	0.50	0.06	0.25	
Acenaphthylene				0.45	0.42	0.32		0.51	0.49	0.40	0.48	0.82	0.56	0.50	0.80		0.39	0.56	0.33	0.53	0.58	0.83	0.72	0.12	0.50	0.08	0.31	0.19
Acenaphthene																								0.12	0.50			
Fluorene	4.45	7.03	8.78	11.97	8.70	9.32	7.79	9.03	13.14	11.03	12.59	15.27	13.87	13.42	15.56	13.29	16.71	13.70	14.83	16.99	16.92	18.87	18.81	0.12	0.50	0.08	0.33	0.48
C1-Fluorene	35.94	31.27	29.79	34.22	27.03	34.91	26.32	24.35	35.98	28.81	34.35	32.78	33.33	29.46	37.92	30.19	30.31	27.55	29.37	30.27	34.63	30.92	30.65	0.12	0.50	0.06	0.24	0.05
C2-Fluorene	21.57	17.03	20.64	19.06	21.77	31.93	14.71	13.66	16.34	12.88	17.01	14.61	16.12	12.83	18.20	12.74	9.56	10.86	10.98	10.38	16.89	11.92	11.23	0.12	0.50	0.06	0.24	0.27
C3-Fluorene																								0.12	0.50			
C4-Fluorene																												
Dibenzothiophene	2.55	2.80	2.00	3.48	3.61	3.16	2.38	3.24	3.44	2.82	3.21	3.30	3.16	2.78	3.49	2.13	1.99	1.97	1.40	2.01	2.94	1.90	1.87	0.12	0.50	0.07	0.27	0.07
C1-Dibenzothiophene	1.63	1.52	1.22	2.09	1.77	2.01	1.43	1.86	1.84	1.45	1.85	2.17	2.01	1.39	2.37	1.49	0.86	1.11	0.94	1.33			0.93	0.12	0.50	0.07	0.27	0.07
C2-Dibenzothiophene	10.43	10.35	7.83	12.49	12.24	13.02	8.41	10.79	10.19	7.95	8.64	9.68	8.09	6.09	9.40	6.30	2.86	4.08	3.34	3.95	9.78	2.10	1.90	0.12	0.50	0.07	0.27	0.07
C3-Dibenzothiophene																												
C4-Dibenzothiophene																								0.12	0.50			
Phenanthrene	41.24	31.70	37.32	40.96	31.05	39.02	28.20	29.14	39.01	29.34	36.82	39.63	40.21	34.48	45.17	35.74	35.73	33.72	32.32	33.49	40.41	35.86	34.23	0.12	0.50	0.08	0.31	0.73
Anthracene	2.83	2.23	1.68	1.94	1.55	1.73	1.58	2.66	2.60	2.43	1.70	2.38	1.75	2.54	1.92	2.70	2.26	2.05	2.52	2.72	3.11	2.33	2.34	0.12	0.50	0.08	0.31	0.43
C1-Phen/Anth	43.09	36.95	41.07	47.56	35.75	39.44	30.47	37.61	39.73	35.40	42.32	39.58	35.94	32.16	24.45	33.41	25.85	29.70	28.48	30.45	39.13	31.56	31.29	0.12	0.50	0.08	0.31	0.72
C2-Phen/Anth	15.55	15.05	22.26	22.59	15.97	14.26	14.24	13.35	16.60	13.15	18.76	20.22	16.05	15.41	16.46	13.52	13.50	13.59	11.31	15.57	13.35			0.12	0.50	0.08	0.31	0.15
C3-Phen/Anth	0.64	0.65			0.74			0.72																0.12	0.50	0.08	0.31	

C4-Phen/Anth	2.77	3.17	2.65	1.11	2.06	2.10	2.35	3.24	1.06	0.93	1.00	1.31	1.30	1.20	1.26	1.56	1.84	1.43	1.92	2.80	3.04	3.51	3.66	0.12	0.50	0.08	0.31	0.15
Fluoranthene	10.25	9.70	10.45	11.74	8.24	13.39	8.85	10.28	13.84	10.50	12.44	18.25	14.91	12.69	21.63	16.82	14.42	16.58	15.34	15.52	23.29	14.86	14.34	0.12	0.50	0.21	0.86	0.43
Pyrene	33.82	29.51	27.69	32.90	18.54	55.32	22.25	28.77	42.52	16.72	27.29	54.81	40.42	21.11	69.03	50.59	19.90	38.70	35.86	36.31	87.48	14.38	14.15	0.12	0.50	0.19	0.77	1.05
C1-Fluoth/Py	8.94	9.25	9.85	10.61	10.15	9.76	7.71	9.52	8.61	8.16	7.97	8.84	7.83	7.92	7.71	7.52	8.11	7.22	7.30	8.35	10.06	9.82	10.10	0.12	0.50	0.19	0.77	0.41
C2-Fluoth/Py																								0.12	0.50	0.19	0.77	
C3-Fluoth/Py																								0.12	0.50	0.19	0.77	
C4-Fluoth/Py																								0.12	0.50	0.19	0.77	
Retene	41.06	42.98	48.03	47.08	36.89	43.76	41.30	38.23	42.91	32.57	43.37	50.01	58.62	43.56	53.50	57.30	52.58	53.01	227.11	52.44	87.04	59.54	56.62	0.12	0.50	0.27	1.08	2.45
Benzo[a]anthracene	2.97	3.59	3.81	3.67	3.92	3.41	2.89	3.27	2.61	2.57	2.52	2.44	2.72	2.07	2.07	1.52	1.48	1.50	1.40	1.40	1.58	1.74	1.76	0.12	0.50	0.15	0.60	0.76
Chrysene	6.51	6.66	7.42	7.98	7.33	6.53	5.44	6.12	5.30	5.06	5.07	5.30	4.27	4.29	4.25	3.48	3.49	2.86	2.63		3.06			0.12	0.50	0.10	0.42	0.34
C1-Chrysene	13.21	20.68	15.29	15.82	15.81	14.78	11.35	14.01	10.98	10.77		10.32	9.41	9.06	8.51	7.76	7.64	6.47	6.36	6.24	6.36	6.78	6.37	0.12	0.50	0.10	0.42	0.48
C2-Chrysene																								0.12	0.50			
C3-Chrysene																								0.12	0.50			
C4-Chrysene																												
Benzo[b]fluoranthene	9.25	10.90	8.37	11.43	8.83	11.56	12.79	15.74	15.79	15.89	14.58	15.93	13.89	13.83	14.15	17.89		11.70	13.07	11.65	11.73	13.27	12.99	0.12	0.50	0.11	0.46	0.34
Benzo[k]fluoranthene	1.89	1.74	7.00	1.48	6.76	1.37	1.14	1.41	1.13	6.42	1.11	1.37	1.32	6.97	7.38	6.90	7.36	1.14	6.49	6.39	6.48	7.47	7.19	0.12	0.50	0.12	0.50	0.20
Benzo[a]Pyrene	2.49	2.64	3.30	3.23	3.46	3.11	2.38	2.96	2.20	2.29	2.18	2.12	2.03	1.98	1.88		1.50							0.12	0.50	0.11	0.43	0.60
Perylene	26.95	28.07	24.28	25.85	24.64	29.15	32.33	32.80	33.98	36.25	37.50	44.19	44.30	45.90	49.57	48.94	54.17	53.84	53.64	54.59	53.73	63.63	70.84	0.12	0.50	0.09	0.35	8.06
Indeno[1,2,3-cd]pyrene	2.50	2.94	3.27	3.25	3.22	3.33	2.83	3.59	3.35	3.31	3.30	3.78	3.63	3.79	4.13	3.35	3.70	3.42	3.45	3.25	3.28	3.51	3.72	0.12	0.50	0.05	0.19	0.21
Dibenzo[a,h]anthracene			2.28		2.41	2.08	1.72	2.10		1.97														0.12	0.50	0.03	0.12	
Benzo[g,h,i]perylene	4.59	5.06	5.39	5.35	5.24	5.69	4.41	5.40	4.93	4.75	5.02	5.10	4.81	4.96	5.09	4.53	4.90	4.36	4.34	4.28	4.24	4.64	4.66	0.12	0.50	0.03	0.11	0.23
Coronene	2.16	2.48	2.67	2.66	2.56	2.78	2.35	2.90	2.74	2.63	3.15	2.82	2.79	2.75	2.86	2.37	2.58	2.30	2.38	2.12	2.04	2.31	2.24	0.12	0.50	0.02	0.10	0.20
$\sum PAH_{Total}$	279.11	262.42	279.36	305.38	256.57	321.55	221.64	253.33	291.68	235	260.21	310.01	277.63	240.93	322.83	273.43	214.36	234.27	233.98	243.88	338.34	216.27	212.91					
$\sum PAH_{Parent}$	125.34	116.5	128.76	139.83	113.28	159.34	104.65	124.22	150.35	115.5	128.31	170.5	147.55	125.41	196.55	158.94	113.83	132.26	133.98	134.54	205.1	119.66	116.78					
$\sum PAH_{Alk}$	153.77	145.92	150.6	165.55	143.29	162.21	116.99	129.11	141.33	119.5	131.9	139.51	130.08	115.52	126.28	114.49	100.53	102.01	100	109.34	133.24	96.61	96.13					
Mass of sediment extracted (g)	5.03	7.46	7.66	7.54	10.54	7.99	8.92	10.05	9.85	11.04	9.71	10.40	12.50	14.36	12.85	14.97	14.74	16.00	16.89	19.91	20.30	20.43	18.90					

Text S3. Compound-specific isotopic analysis (CSIA)

The $\delta^{13}C$ values of several in-house standards (m-terphenyl, o-terphenyl, 5-α-androstane, C_{16} and perylene) were determined using an elemental analyzer (EA) coupled to our PRISM III IRMS system. These compounds were chosen in order to cover the entire mass and isotopic range expected in our samples. Due to a lack of certified isotopic standards for PAHs, only 5-α-androstane had a commercially characterized $\delta^{13}C$ value (-31.6‰). The other standards were characterized on the EA-IRMS to be used as reference values and to check for potential isotopic fractionation in the combustion interface of the GC-C-IRMS system. All standards were injected 8 times in the GC-C-IRMS for three different mass (12.5 ng, 25 ng and 50 ng) to check the linearity of the measurement and the difference from EA-IRMS analysis. The mean standard deviation and the standard deviation to the value obtained with the EA-IRMS measurements are reported in Table S3.

We reported the error associated with the GC-C-IRMS $\delta^{13}C$ measurement as the standard deviation (precision) of triplicate injections of each sediment layer. The precision ranged between 0.0 and 0.4‰ for the co-injected standard (5-α-androstane), between 0.1 and 0.4‰ for dibenzothiophene, between 0.1 and 0.3‰ for C1-alkylated fluorene and between 0.1 and 0.7‰ for retene. The accuracy was established as the mean of the differences between the true value of 5-α-androstane (-31.6‰) and the measured value of 5-α-androstane (-31.1 ±0.5‰, n = 6). All the data points are corrected for the slight shift of the co-injected standard.

To measure the statistical differences between pre-80s and post-80s $\delta^{13}C$ values, we performed a t-test (confidence interval 0.99) using the software R, giving us p-values of 0.00098, 8.98×10^{-5} and 0.29 for DBT, C1-F and retene respectively. According to this test, retene is the only compound not showing any significant isotopic variation during the last century.

Table S3. Isotopic standards used for GC-C-IMRS analysis.

Compound	*Mean $\delta^{13}C$ (‰)*	*1 σ*	*Mean of 1 σ from EA measurement*	*Mass PAH injected*
o-terphenyl	-27.7	0.41	0.58	
C16 *n*-alkane	-29.6	0.60	1.01	
5-α-Androstane	-31.1	0.52	0.57	12.5 ng
m-terphenyl	-27.0	0.70	0.59	
Perylene	-26.3	0.64	1.42	
o-terphenyl	-27.7	0.36	0.63	
C16 *n*-alkane	-29.6	0.50	0.99	
5-α-Androstane	-31.0	0.41	0.64	25 ng
m-terphenyl	-26.8	0.39	0.36	
Perylene	-25.7	0.38	0.81	
o-terphenyl	-27.4	0.38	0.84	
C16 *n*-alkane	-29.6	0.47	1.02	
5-α-Androstane	-30.9	0.43	0.75	50 ng
m-terphenyl	-26.7	0.46	0.49	
Perylene	-25.4	0.53	0.63	

Text S4. Sediment Dating

The activities of ^{210}Pb, ^{137}Cs and ^{214}Pb in ALE sediments were determined by low-background gamma spectrometry in freeze-dried and homogenized sediment samples after at least one month storage in sealed polypropylene vials to achieve secular equilibration of ^{222}Rn and ^{214}Pb with ^{226}Ra.[6] Excess ^{210}Pb ($^{210}Pb_{xs}$) was obtained by subtracting the ^{226}Ra activity (determined by the gamma emissions of its daughter isotope ^{214}Pb) from that of measured ^{210}Pb. Counting efficiencies were determined by preparing dry sediment samples labelled with standard solutions of mixed nuclides. The measured activities were corrected for sample geometry and self-absorption.[7] Similar methodology was used to measure ^{137}Cs and ^{214}Pb in ALD sediments but ^{210}Pb was determined in these samples by measuring its short-lived daughter isotope ^{210}Po.[8-10] The ^{137}Cs in ALD was measured by γ-spectrometry at INRS Eau Terre Environnement (Québec, QC, Canada) and the ^{210}Pb at MyCore Scientific (Deep River, ON, Canada) by α-spectrometry. Five layers in the middle of the core were analyzed at both labs for ^{210}Pb to assess the variability between the different methods. The standard deviation between each pair of measurements was always lower than the error associated with γ-spectrometry, validating the equivalence between both measurements (Table S4).

The dry bulk density was determined as described by Avnimelech et al.[11] using the water and organic carbon contents in each sediment layer, and by assuming that the organic matter content is twice that of organic carbon and that the mineral and organic matter densities are 2.65 and 1.25 g cm^{-3}, respectively.

Table S4. γ-spectrometry and α-spectrometry measurement comparison in 5 sediment layers in ALD.

# layer (cm)	*γ-spectrometry ^{210}Pb activity (Bq/g)*	*α-spectrometry ^{210}Pb activity (Bq/g)*	*γ-spectrometry error (Bq/g)*	*α-spectrometry error (Bq/g)*	*Standard deviation γ/ α*
18-19	0.13965	0.12024	0.01450	0.00697	0.01373
19-20	0.11585	0.11152	0.01430	0.00559	0.00307
20-21	0.09137	0.08677	0.01320	0.00530	0.00326
21-22	0.07470	0.06034	0.01390	0.00428	0.01015
22-23	0.03867	0.02756	0.01290	0.00326	0.00786

Table S5. Interim Sediment Quality Guidelines (ISQG) established by the Canadian Council of Ministers of the Environment[12] compared to the average PAH concentration in surficial sediment (0-5 cm) in ALE and ALD.

PAH	ISQG (µg kg^{-1})	*ALE* (µg kg^{-1})	*ALD* (µg kg^{-1})
Naphthalene	**34.60**	2.90	11.20
Acenaphthylene	**5.87**	0.50	0.20
Acenaphthene	**6.71**	3.80	0.00
Fluorene	**21.20**	11.30	8.20
Phenanthrene	**41.90**	36.70	36.40
Anthracene	**46.90**	4.50	2.00
Fluoranthene	**111.00**	14.50	10.10
Pyrene	**53.00**	43.40	28.50
Benz(a)anthracene	**31.70**	8.40	3.60
Chrysene	**57.10**	10.60	7.20
Benzo(a)pyrene	**31.90**	9.70	3.00
Dibenz(a,h)anthracene	**6.22**	3.00	0.90

Text S5: PAH diagnostic ratios

Two different pools were observed for (An)/(Ph+An) and Fl/(Fl+Py) ratios in ALE (Fig. S1a). The first grouping covers a time period between 1900 to 1980 and shows significant scatter with (An)/(Ph+An) ranging from ~0.17 to 0.23 and Fl/(Fl+Py) ranging from ~0.25 to 0.47. The second pool spans the years 1980 to the present and shows a near linear decrease from ~0.14 to 0.07 for (An)/(Ph+An) and a range of ~0.23 to 0.31 for Fl/(Fl+Py) going towards the petroleum end-member. This cross plot shows similar trends to those found for IcdP/(BghiP+IcdP) vs Fl/(Fl+Py) in ALE, with the main exceptions being that: 1) the chronological trend in the 2000s was not visible, 2) there are two instead of three clusters of data, and 3) the lichen diagnostic ratios are less representative of oil sands particulate input. This poor representability of the lichen (An)/(Ph+An) ratio can be explained by the fact that no anthracene was detected in oil sands.[5] This ratio is therefore likely indicative of some other local PAH emission source such as diesel combustion[13] from the large vehicles operating in the open pit mine areas. In ALD, the diagnostic ratio An/(Ph+An) showed no discernible trends across the entire 23 cm length of the core and thus provided no insight into PAH sources (Fig. S1b). Significant sediment mixing and very low anthracene concentrations (closer to the LoQ than in ALE) were likely the main controlling factors for this scattering.

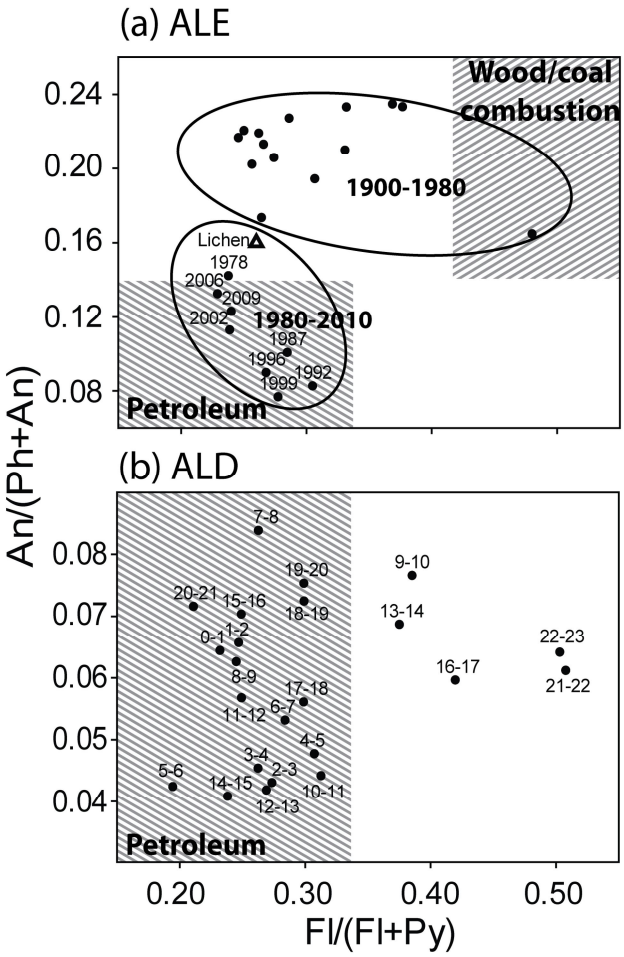

Figure S1. PAH diagnostic ratios cross plot: An/(Ph+An) vs Fl/(Fl+Py) for ALE (a) and ALD (b). The triangle represents a ground-dwelling lichen sample (*C. mitis*) collected close to the main area of bitumen mining activities. The shaded areas represent combustion and petroleum sources[13, 14] and the circled areas correspond to the different pools of sources identified in the sediment core.

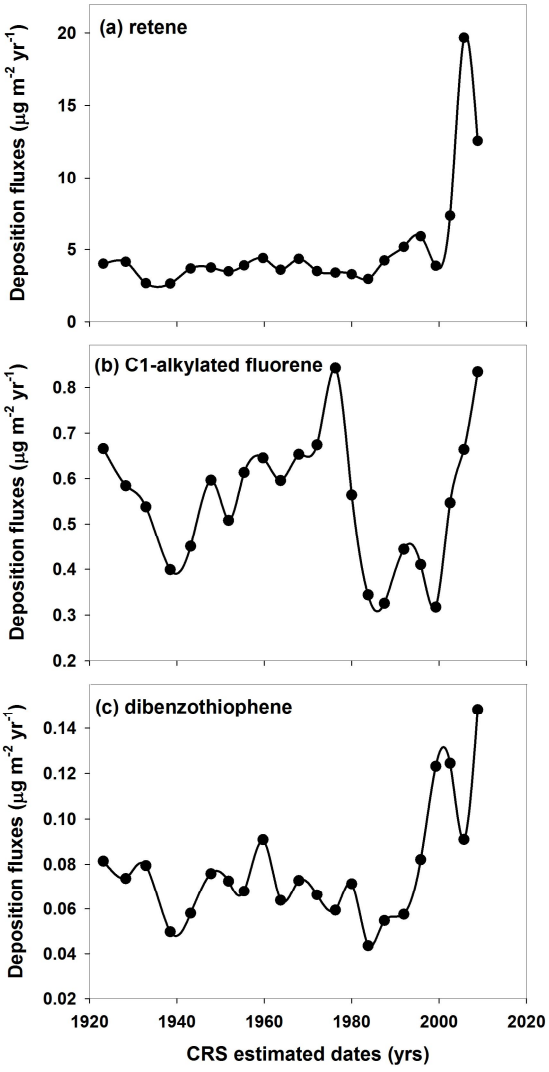

Figure S2. Historical deposition fluxes of (a) retene, (b) C1-alkylated fluorene, and (c) dibenzothiophene in ALE.

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