Supporting information

Airborne Petcoke Dust is a Major Source of Polycyclic Aromatic Hydrocarbons in the Athabasca Oil Sands Region

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SI Text

Chemical Standards

Twenty-three parent PAHs standards (unlabelled) and 16 internal standards (deuterium-labelled) were purchased from Wellington Lab, 15 alkyl PAHs standards were purchased from Norway Chiron, and retene standard was purchased from ChemService in 2013.

Sample Pretreatment

The *Sphagnum* moss was trimmed using a stainless steel knife to obtain a final sample consisting only in the living layer (i.e., green *Sphagnum* plants), then the living layer was reduced in small *Sphagnum* aggregates and foreign plant materials were removed from the moss by hand, using surgical stainless steel tweezers. The peat cores were frozen cut into about 1 cm slices using a stainless steel band saw with stainless steel blades. After cutting, each slice was trimmed (13×13 cm) and sub-samples of different sizes were obtained for various analyses. A sub-sample (13×4 cm) from each slice was used for PAHs analysis. All the moss and peat sample preparation were performed in the peat prep room of the SWAMP lab in the Department of Renewable Resources, University of Alberta.

Moss and peat samples were freeze-dried over 48 hours and milled into fine powder by titanium centrifugal milling (Retsch Ultra Centrifugal Mill, Germany). Prospective source samples (one exposed bitumen sample from outcrops along the Athabasca River, one oil sands ore sample, one fine tailings sample, two delayed petcoke and two fluid petcoke) from the AOSR were also collected and analyzed. Twenty-three snow samples were collected in winter 2015 prior to the major spring melt (Table S1). The snow samples were melted and filtered (GB-140 Glass Fiber Membrane filter, 90 mm diameter, pore size: 0.4 μm). The filters with particles were also freeze-dried for 48 hours.

Accelerated solvent extraction (ASE) was used for target analyte extraction from moss, peat, prospective source samples and snow filters. Glass fiber filter was added at the bottom of the extraction cell, and about 1~3 g of florisil powder (precleaned by dichloromethane and hexane) was added, followed by 1 g of dried moss, peat, 0.1g prospective source samples, or snow filters, to which the internal standard mix was then spiked (10 ng of each). ASE cells were filled with solvent (hexane/dichloromethane 4:1 v:v, Optima™), pressurized to 14 MPa, and heated to 80 °C within 6 min. Pressure and temperature were held for 5 min (static extraction), followed by rinsing with cold solvent (50% of the cell volume) and purging with nitrogen gas for 90 s. This extraction cycle was repeated once. Approximately 40 mL of total extract was then gently concentrated to 1 mL by nitrogen gas evaporation.

Liquid-liquid extraction method was used for snow meltwater samples. The internal standard mix (10 ng of each) was spiked into 500 mL snow water and shaken for 3 minutes; then 50 mL dichloromethane was added and shaken for 3 minutes. The dichloromethane extract was removed and another 50 mL dichloromethane was added and shaken for another 3 minutes again. The dichloromethane extracts were combined (100 mL) and concentrated to 1 mL by nitrogen gas evaporation.

Copper powder and anhydrous sodium sulfate were precleaned by dichloromethane and hexane, and

added into the extract and vortexed for all the sample extracts. Finally, the extract was taken up in 5 mL hexane and re-concentrated to 1 mL.

Solid phase extraction (SPE) was used for cleanup of all the sample extracts. The silica cartridge (Waters, 1g/6cc) was conditioned with 5 mL hexane, then extracts (1mL) were loaded, and 4 mL of hexane was used to wash the extracts tube and loaded (15 mL tube 1 received). Then, PAHs and retene were eluted with 5 mL of hexane/dichloromethane 4:1 (v/v) (15 mL tube 2 received). The extract in tube 2 was concentrated to about 0.2 mL, then 3 mL of hexane was added, and finally was concentrated and diluted with hexane to 200 μL and transferred to vials with glass inserts. These vials were centrifuged and 50 μL of supernatant was transferred into new glass inserts for GC-MS analysis.

Instrumental method for PAHs

GC-MS analysis was by splitless injection of 1 μL from all extracts. Chromatographic separation was accomplished with a DB-5MS column (Agilent; 20 m × 0.18 mm × 0.18 μm) with a helium flow of 1.8 mL min^{-1}. Targeted analytes were analyzed in single ion monitoring (SIM) mode, and concentrations were determined using internal standard. Each sample was injected twice to accommodate the large number of analytes, each with a different temperature program (Table S2). Method 1. Injector program 55 °C, held for 0.4 min, 22 °C min^{-1} to 200 °C, and 6 °C min^{-1} to 280 °C, then 10 °C min^{-1} to 320 °C, held for 2 min, 25 °C min^{-1} to 335 °C, held for 5 min. Method 2. Injector program 55 °C, held for 0.4 min, 22 °C min^{-1} to 200 °C, and 6 °C min^{-1} to 270 °C, then 25 °C min^{-1} to 335 °C, held for 5 min.

Quality Control

A method blank was extracted with each batch of 10 samples to monitor method contamination. One solvent blank (MS grade hexane) was injected after every 10 samples to monitor for possible carryover. The method detection limits (MDL) were defined as the concentration with a signal-to-noise ratio of 3 if the specific analyte was not detected in the blanks. For analytes detected in blanks, MDL was defined as the mean blank concentration plus three times the standard deviation of the blank. As shown in Table S2, MDLs based on ASE sample preparation were generally <10 ng/g based on 1 g dry wt, and MDLs based on liquid-liquid extraction were <5 ng/L based on a 500 mL water sample (Optima™ LC/MS). Results below MDL were substituted by MDL divided by the square root of 2 for statistical comparison among sites. All results were blank corrected using the blank from each batch. Nineteen of the 38 targeted analytes monitored in present study were below the MDL in all the samples (Table S2).

Among the 16 PAHs analyzed in samples, acenaphthylene and acenaphthene were always below MDLs (0.066 and 3.9 ng/g, respectively). Naphthalene (a 2 ring PAH) was detected in all the samples, but was excluded from several analyses due to its higher volatility, mobility, and greater biodegradability.[1,2] Thus, the other 13 detectable PAHs are referred to as $\sum_{13}$PAH.

Triplicate recovery experiments were performed with a mixture of some of the 68 moss samples and peat samples. Native standards (10 ng) and internal standards (10 ng) were spiked to 1 g composite dry moss or peat sample. Native standards (20 ng) and internal standards (10 ng) were spiked into 500 mL Optima™ LC/MS water. The mean recovery was satisfactory for most analytes, except for the some alkyl PAHs, owing to inappropriate internal standards, but these were not detected in moss, peat and

water samples and therefore are not reported (Table S3).

Two internal lab reference peat samples (peat-1 and peat-2) were analyzed with each batch of extractions, and the relative standard deviations (RSD) of this analysis was <20% for most PAHs (Table S4). The analytical procedure was also evaluated by analyzing commercially available certified reference material [International Atomic Energy Agency (IAEA)-159, Sediment; n=8]. The relative deviation between the present data and reference values range from 1.01% (pyrene) to 26.44% (acenaphthylene), thus PAH concentrations measured in the IAEA-159 were acceptable and comparable to the concentrations given by the distributor (Figure S2).

Data Availability and Statistical Analysis

Data for synthetic crude oil production and petcoke inventories from four upgraders in 2013, as well as surface area of fine tailings in the AOSR in 2012 were obtained from Alberta Energy Regulator,[3] and Environment and Sustainable Resource Development, Government of Alberta.[4,5]

Regression and pearson correlations were performed by Microsoft Excel 2010. The independent-sample T test was conducted to compare near-field and far-field sites using IBM SPSS Statistics version 20 (Chicago, IL).

We assume spatial autocorrelation in the moss samples (sites 1-24) and estimate a surface of $\sum_{13}$PAHs in Arcmap 10.3 using ordinary kriging with an optimization model using cross validation. No data transformation was performed and no assumption of anisotropic variation was made.

CMB 8.2 Source Apportionment Modeling

The EPA CMB8.2 model is based on an effective-variance least squares method, and it requires input of the chemical profiles for the ambient environmental data and prospective sources. This model has been successfully used to apportion sources of PAHs in sediment,[6,7] and was used to apportion sources of elements in lichen (H*ypogymnia physodes*) from the near-field (<20 km) in the AOSR.[8]

All default parameters in the model were used, namely, iteration delta 20; maximum source uncertainty 20%; minimum source projection 0.95. To eliminate the physically impossible negative source contributions, the “source elimination” option was chosen.

The separation of benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[j]fluoranthene with GC are always incomplete, thus these were combined in the CMB model. Furthermore, due to the volatility and biodegradability of naphthalene, this compound was not used as input to the model for any sample or source.

The estimated delayed petcoke contribution to individual metals in moss (Table S10) was calculated by the following 3 equations.

$$\text{Delayed petcoke in the moss (g/g)} = \frac{\text{delayed petcoke contribution (\%)} \times \text{PAHs in the moss (ng/g)}}{\text{PAHs in the delayed petcoke (ng/g)}} \quad (1)$$

Metals from delayed petcoke in moss (ng/g) = metals in the delayed petcoke (ng/g) × delayed petcoke in the moss (g/g) (2)

$$\text{Delayed petcoke contribution for metals in moss (\%)} = \frac{\text{metals from delayed petcoke in the moss (ng/g)}}{\text{metals in the moss (ng/g)}} \times 100\% \quad (3)$$

The data "PAHs in the delayed petcoke" in Equation 1 was 22900 ng/g (Table S8), and the estimated delayed petcoke in moss by Equation 1 was shown in Table S9. The data "metals in the delayed petcoke" in Equation 2 was shown in Table S10. The data "metals in the moss" in Equation 3 was cited from Shotyk et al.[9]

SEM-EDS methods

Particles from dried snow filters and prospective authentic source samples, were transferred to double sided adhesive conductive tape for SEM analysis. These were carbon coated by thermal evaporation (Leica EM SCD005) before analysis by a Zeiss EVO MA 15 LaB_6 filament SEM. The backscattered images were taken using a Si diode detector and EDS spectra were acquired with a peltier-cooled 10 mm^2 Bruker Quantax 200 Silicon drift detector with 123 eV resolution.

Radiocarbon Measurement and Age Model

Between 5 and 7 samples from each peat core were analyzed for radiocarbon. Table S5 outlines the details of plant macrofossil specimens analyzed for ^{14}C dating by accelerator mass spectrometry (AMS). These were pre-treated at the University of Alberta following standard acid–base–acid procedures: solutions were heated to 70°C: 30 min in 1M HCl, 60 minutes in 1M NaOH with solution changed until clear, 30 min 1 M HCl, and rinsed with room-temperature ultrapure water until pH neutral. Secondary standards were also pre-treated concurrently (non-finite-age wood (AVR-PAL-07 and middle Holocene wood (FIRI-F standard) material; all values were within normal range). Pre-treated samples were graphitized and analysed at the Keck-Carbon Cycle AMS facility (University of California, Irvine). The resulting ^{14}C ages were calibrated using Bomb13NH1 and IntCal13 calibration curves (as appropriate) within Oxcal v4.2.[10-12]

The ^{14}C ages for each site were used to construct age-depth models (Figure S3) using the Oxcal *P_Sequence* model with 1 year resolution.[13] Median values for the 68.2% range were plotted as the age depth model for Figure 2 in the main text – associated errors are shown here (Table S5).

A radiocarbon date is an estimate of the ^{14}C activity of a sample representing the synthesis of atmospheric CO_2 into the tissue of the organism (in this case plants) prior to death. The calibration curve which converts ^{14}C activity into calibrated dates is based on a non-monotonic curve developed from measurements of ^{14}C activity against known age, primarily tree rings for the last 12,000 years. The shape of that curve strongly affects the resulting calibration and that can be seen in the radiocarbon dates (and ranges) presented in this paper.

Age ranges for the pre-bomb interval (prior to the 1950s) are strongly affected by the relatively flat nature of the calibration curve during that time due to the Suess effect (burning of fossil fuels that has produced an excess of ^{12}C into the atmosphere following the industrial revolution). This results in some portions of the calibration curve[11] having multiple intercepts at 1 and 2 sigma and relatively broad ranges despite precise analytical measurements of ^{14}C activity. For the post-bomb ages, which measure the quickly decreasing excess ^{14}C activity following reduction in above ground nuclear

testing, the curve is very steep and thus ages are precise. The dates for this interval can typically be limited to a single growing season, thus we have much higher precision for the post-bomb interval than the immediately pre-bomb time frame.

Table S1. Sample collection detailed information.

Samples	Collection date	Sampling sites	Number
Mosses	July 20 and 21, 2013	Sites 1-20 around the AOSR	60 (in triplicate)
Mosses	August 6 and 7, 2013	Site 21 (Anzac-ANZ) and site 22 (JPH-4)	6 (in triplicate)
Mosses	October 16 and 17, 2013	Site 23 (Mildred-MIL) and site 24 (Macky-McK)	2
Peat core*	August 6, 2013	Site 21 (ANZ)	40 layers
Peat core*	August 7, 2013	Site 22 (JPH-4)	40 layers
Peat core*	October 16, 2013	Site 23 (MIL)	40 layers
Peat core*	October 17, 2013	Site 24 (McK)	41 layers
Mosses	September 18, 2014	Site 28 reference (Utikuma-UTK)	3 (in triplicate)
Mosses	July 24, 2014	Site 29 reference (Seba-SEB)	3 (in triplicate)
Mosses	October 30, 2014	Site 30 reference (Elk Island National Park-EINP)	3 (in triplicate)
Snow core	March 10, 2015	Site 22, 23 and 24	9 (in triplicate)
Snow core	March 11, 2015	Site 21 and site 25 (Mcmurray-McM)	6 (in triplicate)
Snow	March 11, 2015	Site 26 reference-Along Anzac railway	1
Snow	March 14, 2015	Site 27 reference (Edmonton-EDM)	3 (in triplicate)
Naturally exposed bitumen		Along the Athabasca river	1
Oil sands ore		Mines in the AOSR	1
Delayed petcoke 1		AOSR	1
Delayed petcoke 2		AOSR	1
Fluid petcoke 1		AOSR	1
Fluid petcoke 2		AOSR	1
Fine tailings		AOSR	1

*The actual layers for the sites 21-24 peat cores are 97, 71, 59 and 81, respectively. Only the top 40-41 layers for these peat cores are analyzed in the present study.

Table S2. Target ions, qualifier ions, and internal standards used for each analyte in GC-MS analysis. Nineteen of the 38 targeted analytes monitored in the present study were below the MDL (italics) in all moss, peat and snow samples.

Target analytes	Target ions (m/z)	Qualifier ions (m/z)	Internal Standards	MDL for ASE method (ng/g)	MDL for liquid-liquid method (ng/L)	GC-MS Method[†]
Naphthalene	128	102	Naphthalene-d8	7.7	3.6	1
1-Methylnaphthalene	*141*	*115*	*Naphthalene-d8*	*43*	*0.018*	*1*
1-Ethylnaphthalene	*141*	*156*	*Naphthalene-d8*	*1.9*	*0.019*	*1*
2-n-Propylnaphthalene	*141*	*170*	*Naphthalene-d8*	*11*	*0.024*	*1*
Acenaphthylene	*152*	*76*	*Acenaphthene-d10*	*0.066*	*0.14*	*2*
Acenaphthene	*153*	*76*	*Acenaphthene-d10*	*3.9*	*2.3*	*2*
Fluorene	165	139	Fluorene-d10	3.2	2.6	1
1-Methylfluorene	165	180	Fluorene-d10	4.0	0.78	1
9-Ethylfluorene	*165*	*194*	*Fluorene-d10*	*1.5*	*0.033*	*1*
9-n-Butylfluorene	*165*	*222*	*Fluorene-d10*	*0.16*	*0.065*	*1*
Phenanthrene	178	152	Phenanthrene-d10	5.0	4.8	2
1-Methylphenanthrene	192	95	Phenanthrene-d10	0.27	0.11	2
3,6-Dimethylphenanthrene	206	191	Phenanthrene-d10	0.17	0.070	2
9-n-Butylphenanthrene	*191*	*234*	*Phenanthrene-d10*	*3.7*	*0.88*	*2*
Anthracene	178	152	Anthracene-d10	0.66	0.58	2
Fluoranthene	202	101	Fluoranthene-d10	0.76	1.2	1
Pyrene	202	101	Pyrene-d10	1.9	1.5	1
1-Methylpyrene	216	189	Pyrene-d10	0.12	0.050	1
1-Ethylpyrene	*215*	*230*	*Pyrene-d10*	*0.13*	*0.052*	*1*
1-n-Butylpyrene	*215*	*258*	*Pyrene-d10*	*0.12*	*0.057*	*1*
Cyclopenta[c,d]pyrene	*226*	*113*	*Benz[a]anthracene-d12*	*0.15*	*0.031*	*2*
Benz[a]anthracene	228	113	Benz[a]anthracene-d12	0.13	0.052	2
1-Methylbenz[a]anthracene	*242*	*228*	*Benz[a]anthracene-d12*	*0.11*	*0.046*	*2*
Chrysene	228	113	Chrysene-d12	0.46	0.072	2
6-Ethylchrysene	*241*	*256*	*Chrysene-d12*	*0.18*	*0.073*	*2*
6-n-Butylchrysene	*241*	*284*	*Chrysene-d12*	*0.18*	*0.073*	*2*
5-Methylchrysene	*242*	*120*	*Chrysene-d12*	*0.24*	*0.097*	*2*
Benzo[b]fluoranthene	252	126	Benzo[b]fluoranthene-d12	0.81	1.5	1
Benzo[k+j]fluoranthene	252	126	Benzo[k]fluoranthene-d12	0.35	0.17	1
Benzo[a]pyrene	252	126	Benzo[a]pyrene-d12	0.43	0.17	1
Indeno[1,2,3-cd]pyrene	276	138	Indeno[1,2,3-cd]pyrene-d12	0.15	0.060	1
Benzo[g,h,i]perylene	276	138	Benzo[g,h,i]perylene-12	0.15	0.061	1
Dibenz[a,h]anthracene	278	138	Dibenz[a,h]anthracene-d14	0.39	0.094	1
Dibenzo[a,l]pyrene	*302*	-	*Dibenzo[a,i]pyrene-d14*	*0.31*	*0.072*	*1*
Dibenzo[a,e]pyrene	*302*	-	*Dibenzo[a,i]pyrene-d14*	*0.24*	*0.061*	*1*
Dibenzo[a,i]pyrene	*302*	-	*Dibenzo[a,i]pyrene-d14*	*0.34*	*0.087*	*1*
Dibenzo[a,h]pyrene	*302*	-	*Dibenzo[a,i]pyrene-d14*	*0.43*	*0.093*	*1*
Retene	219	234	Benz[a]anthracene-d12	0.75	0.30	2

Table S3. Internal standard corrected recovery of analytes in moss, peat and water.

Native Standards	Moss sample (N=3)[†]		Peat sample (N=3)[‡]		Optima™ LC/MS water	
	Mean recovery %	SD %	Mean recovery %	SD %	Mean recovery %	SD %
Naphthalene	118.0	30.0	145.3	45.9	109.5	9.3
1-Methylnaphthalene[*]	*159.3*	*28.0*	*154.7*	*22.5*	61.0	3.5
1-Ethylnaphthalene	*280.7*	*30.4*	*176.7*	*13.3*	61.2	3.1
2-n-Propylnaphthalene	*201.3*	*40.5*	*152.0*	*22.7*	60.3	4.4
Acenaphthylene	116.7	6.4	108.0	5.3	99.6	8.8
Acenaphthene	111.3	25.8	106.0	7.2	97.8	5.9
Fluorene	95.3	11.0	78.0	6.0	91.6	3.6
1-Methylfluorene	95.3	13.0	106.0	13.1	85.3	5.7
9-Ethylfluorene	68.7	11.7	66.0	7.2	74.6	4.7
9-n-Butylfluorene	93.3	9.5	113.3	8.3	67.0	6.0
Phenanthrene	80.0	18.0	96.7	5.0	114.5	6.4
1-Methylphenanthrene	83.3	7.6	90.0	4.0	127.3	3.4
3,6-Dimethylphenanthrene	102.7	8.3	118.0	3.5	179.0	15.9
9-n-Butylphenanthrene	116.0	4.0	120.7	7.6	246.2	26.8
Anthracene	104.0	3.5	92.7	4.2	102.9	5.8
Fluoranthene	106.0	12.2	96.7	4.2	101.6	4.7
Pyrene	114.0	15.6	102.0	5.3	106.2	6.2
1-Methylpyrene	88.0	8.7	84.0	2.0	93.7	5.1
1-Ethylpyrene	104.0	10.4	97.3	3.1	105.5	8.2
1-n-Butylpyrene	*146.7*	*15.1*	*136.7*	*3.1*	128.6	9.6
Cyclopenta[c,d]pyrene	120.0	9.2	128.7	8.3	83.7	4.2
Benz[a]anthracene	87.3	10.3	101.3	6.1	87.5	4.3
1-Methylbenz[a]anthracene	51.3	5.8	57.3	3.1	61.2	3.6
Chrysene	70.0	12.2	57.3	3.1	112.4	9.6
6-Ethylchrysene	58.7	6.4	66.0	3.5	103.4	0.8
6-n-Butylchrysene	72.7	8.1	71.3	1.2	98.8	5.6
5-Methylchrysene	92.0	8.7	94.0	8.7	143.6	4.4
Benzo[b]fluoranthene	60.0	3.5	69.3	1.2	82.9	6.1
Benzo[k+j]fluoranthene	91.3	9.5	94.0	5.3	110.8	7.6
Benzo[a]pyrene	87.3	11.0	84.7	1.2	93.7	6.0
Indeno[1,2,3-cd]pyrene	101.3	11.0	98.7	6.4	107.9	5.2
Benzo[g,h,i]perylene	103.3	7.6	98.0	7.2	108.1	6.6
Dibenz[a,h]anthracene	112.7	7.0	105.3	12.1	115.0	7.9
Dibenzo[a,l]pyrene	100.7	8.3	113.3	11.0		
Dibenzo[a,e]pyrene	95.3	8.1	106.7	9.0		
Dibenzo[a,i]pyrene	100.7	6.1	103.3	6.1		
Dibenzo[a,h]pyrene	108.7	6.4	115.3	11.0		
Retene	86.3	13.9	80.9	7.1	75.2	2.6

[*]Analytes shown in italics had unacceptably high recovery, owing to inappropriate internal standards, but these were not detected in moss and peat samples. [†]Moss used here was a composite from some of the 68 moss samples (6B, 7B, 7C, 8A, 8B, 9A, 9B, 9C, 10A, 10B, 18A, 18C, 19B, 20A, 20B). [‡]Peat used here is a composite from various layers of JPH-4 peat core (51-70) and ANZ core (81-95).

Table S4. Precision of analysis for an internal laboratory reference peat sample (peat-1and peat-2) analyzed repeatedly on different days.

Analytes	Concentration of peat-1 (ng/g)												Concentration of peat-2 (ng/g)								
	1	2	3	4	5	6	7	8	9	Mean (ng/g)	SD (ng/g)	RSD (%)	1	2	3	4	5	6	Mean (ng/g)	SD (ng/g)	RSD (%)
Naphthalene	54.96	54.63	56.73	52.50	59.36	51.96	47.58	57.44	60.05	55.02	3.94	7.16	81.26	88.30	63.30	60.44	104.10	89.03	81.07	16.66	20.54
Acenaphthylene	9.86	11.66	11.28	11.71	13.04	13.42	12.48	13.71	14.19	12.37	1.37	11.10	11.02	9.07	11.72	12.08	13.55	13.40	11.81	1.66	14.05
Acenaphthene	86.04	90.02	92.00	95.38	103.39	90.78	80.36	84.78	89.34	90.23	6.60	7.32	58.04	74.05	51.38	48.31	66.99	65.03	60.63	9.84	16.23
Fluorene	18.72	18.19	24.64	22.44	22.95	22.36	21.02	24.84	24.97	22.24	2.52	11.33	9.92	12.43	11.42	11.00	9.90	10.02	10.78	1.03	9.53
Phenanthrene	106.38	101.77	101.10	98.01	111.50	93.45	88.16	103.40	100.60	100.48	6.84	6.81	72.29	78.95	58.59	56.19	85.94	80.08	72.01	12.15	16.87
Anthracene	3.92	3.75	3.58	3.71	3.34	3.27	2.91	3.82	3.87	3.57	0.33	9.37	4.14	5.86	3.39	3.30	5.73	6.29	4.79	1.33	27.84
Fluoranthene	8.40	7.73	8.03	7.65	8.42	7.64	6.87	8.32	8.46	7.95	0.53	6.64	7.42	8.86	6.18	6.06	8.40	8.89	7.63	1.29	16.89
Pyrene	5.70	5.30	5.48	5.58	5.92	4.97	4.76	5.69	5.34	5.41	0.37	6.81	6.12	7.44	5.19	5.02	8.66	7.13	6.59	1.41	21.39
Benz[a]anthracene	1.82	1.92	2.25	2.70	1.84	1.61	1.56	3.05	2.68	2.16	0.54	24.81	4.19	2.74	3.05	3.09	2.74	2.48	3.05	0.60	19.75
Chrysene	8.55	10.50	6.45	7.09	11.25	10.39	8.93	7.02	6.86	8.56	1.82	21.23	5.41	4.90	4.41	4.26	5.32	4.99	4.88	0.47	9.58
Benzo[b]fluoranthene	5.70	5.98	6.44	6.25	7.41	6.13	6.65	7.28	6.07	6.43	0.58	9.03	2.82	3.48	2.46	3.13	3.89	4.01	3.30	0.61	18.43
Benzo[k+j]fluoranthene	3.75	3.54	3.48	4.23	3.45	3.17	2.87	4.12	3.69	3.59	0.43	11.90	1.73	2.36	2.58	1.78	3.50	2.73	2.45	0.66	26.87
Benzo[a]pyrene	4.35	3.82	4.28	4.08	5.23	4.33	3.70	4.27	3.99	4.23	0.44	10.46	2.01	2.94	2.14	1.97	2.63	3.66	2.56	0.66	25.76
Indeno[1,2,3-cd]pyrene	8.15	8.38	7.76	7.50	10.09	10.69	7.95	9.36	8.69	8.73	1.10	12.55	4.78	5.34	4.10	3.88	4.09	6.19	4.73	0.90	18.99
Benzo[g,h,i]perylene	8.54	8.03	6.92	6.59	7.33	7.01	7.02	8.55	7.29	7.48	0.72	9.68	4.53	5.01	3.88	3.43	3.58	3.61	4.01	0.63	15.67
Dibenz[a,h]anthracene	2.58	2.27	2.58	2.51	2.47	1.79	2.40	2.37	2.18	2.35	0.25	10.57	0.78	0.59	0.57	0.51	1.05	0.64	0.69	0.20	28.67
Retene	3.45	2.99	2.23	2.89	2.74	2.54	1.84	3.09	2.68	2.72	0.48	17.57	4.23	5.28	3.72	4.08	6.43	6.17	4.99	1.15	22.99
1-Methylfluorene	1.02	1.42	1.19	1.01	1.85	1.39	1.34	1.80	1.91	1.44	0.35	24.10	1.62	1.50	1.69	1.46	2.02	2.05	1.72	0.26	14.80
1-Methylphenanthrene	2.09	2.10	2.14	2.16	2.22	2.00	1.92	2.03	2.26	2.10	0.11	5.11	3.51	3.77	2.85	2.82	3.51	4.03	3.42	0.49	14.27
3,6-Dimethylphenanthrene	0.35	0.50	0.25	0.24	0.50	0.44	0.40	0.39	0.30	0.37	0.10	25.63	0.72	0.42	0.60	0.63	0.53	0.49	0.57	0.11	18.56
1-Methylpyrene	0.22	0.21	0.18	0.19	0.20	0.16	0.19	0.16	0.19	0.19	0.02	10.70	0.72	0.81	0.71	0.70	1.00	0.79	0.79	0.11	14.44

Table S5. Radiocarbon dates from the four peat cores (ANZ, JPH4, MIL and McK) and their calibrated & modelled ages (Oxcal v4.2).

Sample ID	UCIAMS Laboratory code	Depth (cm)	Description	Weight (mgC)	Fraction modern		^{14}C age (BP)		Calibrated age (cal BC/AD)				Modelled age (cal BC/AD)	
									68.2% range		95.4% range		68.2% range	Median
ANZ #15	154027	-14.98	*Sphagnum* stems	15.1	1.1521	0.0023	---	---	1990-1991	---	1957-1958	1989-1991	1990-1991	1990
ANZ #20	154026	-19.20	*Sphagnum* stems	11.8	1.2131	0.0022	---	---	1960-1961	1984-1985	1959-1961	1983-1985	1984-1985	1985
ANZ #25	154025	-23.75	*Sphagnum* stems	11.2	1.3133	0.0025	---	---	1978-1979	---	1962	1977-1979	1977-1979	1978
ANZ #30	154024	-28.45	*Sphagnum*, Ericaceae leaves	9.9	1.4155	0.0025	---	---	1962	1974	1962-1963	1973-1974	1973-1975	1974
ANZ #40	142039	-38.62	Twig material		---	---	170	20	1669-1682; 1736-1780; 1799-1805	1935-1944	1665-1693; 1727-1785; 1793-1813	1919-	1665-1685; 1730-1785; 1795-1810	1765
JPH4 #5	154012	-4.31	*Sphagnum*, *Picea* needles	1.5	1.2789	0.0023	---	---	1979-1980	---	1959; 1961-1962	1979-1980; 1981	1979-1981	1980
JPH4 #10	154011	-9.08	*Sphagnum* stems	4.3	1.7993	0.0033	---	---	1965	---	1963-1965	---	1964-1965	1964
JPH4 #14	154009	-12.89	*Sphagnum* stems	6.4	1.2479	0.0023	---	---	1981-1982	---	1959; 1961-1962	1980-1982	1959-1962	1961
JPH4 #20	154008	-18.93	*Sphagnum* stems, *V. oxycoccos* charred leaves, *Picea* charred needles	4.2	---	---	95	15	1698-1724	1815-1835; 1878-1395; 1903-1917	1694-1728	1812-1919	1695-1725; 1815-1835; 1875-1920	1845
JPH4 #30	142066	-28.65	*Sphagnum* stems		---	---	490	40	1411-1445	---	1324-1346	1393-1464	1415-1445	1430
JPH4#39-40	152359	-38.30	*Sphagnum* stems, Conifer/Ericaceae bark, *Carex* seeds, *Picea* charred needles	4.1	---	---	605	20	1306-1329; 1341-1363	1385-1396	1299-1370	1380-1404	1300-1330; 1340-1365; 1385-1395	1340
MIL #10	154023	-10.82	*Sphagnum* stems	6.5	1.1235	0.0020	---	---	1993-1995	---	1957-1958	1993-1995	1994-1995	1994
MIL #15	154022	-16.24	*Sphagnum*, Ericaceae leaves	5.3	1.1843	0.0021	---	---	1958-1959	1986-1988	1958-1959	1986-1988	1987-1988	1987
MIL #20	154021	-21.78	*Sphagnum* stems	5.5	1.3382	0.0024	---	---	1977	---	1976-1977	1978	1976-1978	1977
MIL #25	154018	-27.17	*Sphagnum* stems	3.6	1.2256	0.0022	---	---	1959-1960; 1961	1983-1984	1959-1962	1982-1985	1959-1961	1960
MIL #30	154017	-32.56	*Sphagnum* stems	2.5	1.0587	0.0021	---	---	2006-2008	2009-2014	1956	2005-2014	1956-1957	1957
MIL #35	154016	-38.10	*Sphagnum* stems	2.4	---	---	25	15	1896-1904	---	1891-1907	---	1895-1905	1900
MIL #40	142040	-43.77	Bark of twigs, twig, woody fragments, seeds		---	---	110	20	1694-1710; 1718-1727	1813-1890; 1910-1917	1685-1733	1807-1896; 1903-1928	1690-1730; 1810-1885	1825
McK #10	154007	-11.76	*Sphagnuv* stems	12.2	1.1453	0.0025	---	---	1990-1992	---	1957-1958	1990-1992	1990-1992	1991
McK #15	154006	-17.39	*Sphagnum* stems	8.7	1.2336	0.0022	---	---	1960	1982-1983	1959-1960; 1961-1962	1982-1983	1982-1984	1983
McK #20	154005	-22.96	*Sphagnum* stems	10	1.5258	0.0033	---	---	1970	1971	1969-1971	---	1969-1971	1970
McK #25	154004	-28.58	*Sphagnum*, *Rhododendron* leaves	5.2	1.7272	0.0031	---	---	1966	---	1965-1966	---	1965-1966	1965
McK #40	142064	-45.92	*Sphagnum* stems and leaves		---	---	280	20	1528-1551	1634-1651	1521-1576; 1584-1591	1626-1662	1525-1555; 1630-1650	1560

Table S6. Profiles of PAHs (fractions) in various source samples.

Source of PAHs	FLR	PHE	ANT	FLRT	PYR	BaA	CHRY	BbkjFC	BaP	IcdP	DahA	BghiP	Reference
Samples Analyzed in this Study													
Delayed Petcoke1	0.005	0.074	0.035	0.023	0.066	0.067	0.275	0.026	0.277	0.019	0.035	0.098	
Delayed Petcoke2†	0.008	0.128	0.035	0.030	0.086	0.059	0.243	0.024	0.188	0.034	0.057	0.108	
Naturally Exposed Bitumen†	0.005	0.006	0.010	0.014	0.135	0.003	0.533	0.078	0.046	0.052	0.023	0.094	
Oil Sands Ore†	0.002	0.059	0.066	0.010	0.258	0.043	0.223	0.064	0.095	0.053	0.043	0.084	
Dried Fine Tailings†	0.033	0.319	0.025	0.021	0.144	0.047	0.243	0.046	0.047	0.020	0.011	0.044	
Samples from Literature on the AOSR													
Fire Ash*,†	0.123	0.417	0.061	0.074	0.098	0.005	0.049	0.098	0.005	0.005	0.005	0.061	[14]
Haul Road Dust*,†	0.011	0.521	0.002	0.002	0.062	0.034	0.085	0.108	0.028	0.068	0.002	0.076	[14]
Upgrader Diverter Stack†	0.027	0.635	0.145	0.043	0.093	0.000	0.051	0.003	0.002	0.000	0.000	0.000	[15]
Generic Samples from Literature													
Diesel Engine†	0.002	0.244	0.036	0.260	0.171	0.028	0.090	0.051	0.027	0.026	0.039	0.027	[6]
Power Plant	0.014	0.155	0.018	0.174	0.152	0.108	0.208	0.059	0.038	0.028	0.006	0.042	[6]
Residential	0.003	0.348	0.073	0.225	0.089	0.046	0.067	0.078	0.035	0.019	0.000	0.016	[6]
Coke Oven	0.022	0.079	0.022	0.084	0.085	0.121	0.130	0.214	0.109	0.041	0.017	0.077	[6]
Coal-related	0.011	0.177	0.036	0.150	0.124	0.094	0.131	0.126	0.065	0.035	0.008	0.043	[6]
Gasoline Engine	0.001	0.031	0.008	0.151	0.263	0.069	0.100	0.123	0.063	0.035	0.016	0.140	[6]
Traffic Tunnel	0.014	0.106	0.021	0.105	0.126	0.065	0.103	0.132	0.075	0.097	0.043	0.112	[6]
Traffic-related	0.006	0.170	0.027	0.172	0.177	0.048	0.099	0.091	0.050	0.057	0.031	0.073	[6]

*Fire ash and haul road dust data are extrapolated from Figure 17.5 in *Alberta Oil Sands: Energy, Industry and the Environment*, thus some error is anticipated.

†These 8 profiles were used for the model in the present study.

Table S7. Concentration of target analytes in moss samples from the AOSR (ng/g).

	NAP	FLR	PHE	ANT	FLRT	PYR	BaA	CHRY	BbF	BkjF*	BaP	IcdP	BghiP	DahA	**$\sum_{13}$PAHs**	RET	1-mFLR	1-mPHE	3,6-dPHE	1-mPYR	**∑alkyl-PAH**	**Total PAH**	**∑alkyl-PAH / $\sum_{13}$PAH**
DF (%)*	94	79	100	100	100	100	100	100	79	81	97	94	100	100	---	100	100	100	100	100	--	--	--
1	31.4	9.99	45.3	3.55	3.40	5.17	3.15	8.56	1.84	0.397	3.11	0.703	1.85	3.10	90.1	4.24	29.0	5.17	1.81	1.29	37.3	159	0.414
2	22.4	6.68	35.3	4.35	3.84	8.56	7.05	13.9	2.94	0.806	5.75	1.34	4.45	3.46	98.4	2.88	22.5	6.49	2.79	1.63	33.4	154	0.339
3	5.41	3.18	14.0	0.966	2.16	2.58	0.436	1.50	0.569	0.285	0.674	0.248	0.782	1.36	28.7	2.06	15.0	3.49	1.01	0.572	20.1	54.2	0.700
4	10.8	5.18	21.9	1.67	2.71	2.68	0.420	1.36	0.678	0.247	0.462	0.179	0.517	0.934	38.9	2.08	22.3	4.19	1.04	0.330	27.9	77.6	0.717
5	12.8	6.08	33.3	2.58	2.56	3.24	0.841	2.26	0.691	0.528	0.851	0.306	0.811	1.11	55.2	2.17	26.0	5.81	1.46	0.455	33.7	102	0.611
6	29.7	4.73	31.3	2.49	3.60	3.38	2.02	5.39	1.57	0.398	2.24	0.288	0.938	4.11	62.5	3.63	37.7	5.68	1.81	0.947	46.1	138	0.738
7	25.9	6.59	31.0	2.60	2.42	3.67	1.77	9.25	1.45	0.346	1.78	1.06	2.27	2.09	66.3	4.91	35.7	4.03	1.77	0.739	42.2	134	0.637
8	17.4	4.64	22.8	2.01	2.14	2.95	2.34	5.53	1.10	0.371	1.71	0.711	1.71	5.80	53.8	2.67	35.2	5.84	1.35	0.620	43.0	114	0.799
9	16.5	5.99	40.2	4.61	3.09	5.68	4.49	11.5	2.02	0.558	3.87	1.23	3.16	3.69	90.1	3.33	35.9	9.35	3.10	1.01	49.4	156	0.548
10	28.6	4.48	37.4	3.31	5.53	5.24	2.69	7.25	0.666	0.512	2.68	1.03	2.63	3.66	77.1	2.03	34.3	6.52	1.79	0.777	43.4	149	0.563
11	17.3	8.55	44.2	3.24	4.42	3.97	1.29	4.22	0.780	0.533	1.18	0.543	1.23	4.52	78.7	5.92	34.1	6.85	2.16	0.565	43.7	140	0.555
12	22.3	10.4	51.3	4.04	4.51	5.22	2.22	7.27	1.09	0.731	2.16	0.933	2.58	5.08	97.5	7.51	40.1	7.94	2.40	0.950	51.4	171	0.527
13	39.8	8.19	37.2	2.33	3.11	3.92	1.01	4.47	1.94	0.290	1.36	0.283	0.709	3.40	68.2	2.10	37.3	4.76	1.56	0.755	44.4	152	0.651
14	15.3	7.36	40.0	2.97	3.56	3.25	1.07	2.71	1.03	0.486	1.77	0.478	0.890	11.2	76.8	4.44	29.5	5.56	1.39	0.472	36.9	129	0.480
15	36.4	2.66	51.8	5.52	13.6	12.1	3.21	4.97	0.662	0.375	1.98	0.661	1.99	3.69	103	5.23	9.26	5.13	2.23	0.650	17.3	157	0.168
16	12.2	5.72	28.1	2.79	2.76	2.99	2.05	5.34	0.954	0.733	1.87	0.522	1.81	5.94	61.6	5.88	27.8	4.78	1.15	0.585	34.3	108	0.557
17	21.4	2.26	44.4	4.25	5.92	8.13	4.50	7.07	2.02	0.875	4.88	1.35	3.56	5.50	94.7	5.85	7.17	5.35	2.43	1.53	16.5	133	0.174
18	14.7	4.90	34.8	3.66	3.35	5.30	5.06	11.9	2.25	1.01	4.43	0.708	4.45	5.49	87.3	5.60	14.3	6.13	1.95	1.04	23.4	125	0.268
19	26.6	4.99	66.2	13.3	7.39	21.7	29.3	35.8	5.82	2.61	26.5	7.29	21.7	17.0	260	5.82	23.2	14.8	7.67	4.65	50.3	336	0.193
20	16.9	3.21	37.6	3.13	3.58	4.02	2.02	4.70	1.34	0.646	2.40	0.496	0.948	8.58	72.7	7.61	8.80	4.46	1.64	0.594	15.5	105	0.213
21 (ANZ)	25.9	3.49	42.8	4.05	5.21	6.14	4.08	8.65	2.02	0.898	3.99	1.22	2.36	6.05	91.0	2.27	8.23	4.98	1.97	0.947	16.1	133	0.177
22 (JPH-4)	20.3	2.26	46.8	3.99	4.66	6.16	3.82	10.5	1.68	0.894	3.45	1.45	2.89	8.34	96.9	4.56	5.74	6.56	2.70	1.04	16.0	133	0.165
23 (MIL†)	23.8	3.37	53.2	16.8	12.9	36.5	34.3	94.2	4.80	4.48	39.1	15.5	43.0	30.5	389	4.51	30.9	18.1	8.10	7.58	64.7	477	0.166
24 (McK†)	20.9	2.26	16.1	4.10	6.26	18.4	11.6	36.7	0.905	1.76	9.43	4.47	10.2	12.4	135	19.2	12.3	6.54	4.34	3.36	26.5	182	0.196

*DF, detection frequency (%). †Only one sample was analyzed. Naphthalene (NAP), Fluorene (FLR), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLRT), Pyrene (PYR), Benz[a]anthracene (BaA), Chrysene (CHRY), Benzo[b]fluoranthene (BbF), Benzo[k+j]fluoranthene (BkjF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IcdP), Benzo[g,h,i]perylene (BghiP), Dibenz[a,h]anthracene (DahA), 1-Methylfluorene (1-mFLR), 1-Methylphenanthrene (1-mPHE), 3,6-Dimethylphenanthrene (3,6-dPHE), 1-Methylpyrene (1-mPYR). *Benzo[k]fluoranthene and Benzo[j]fluoranthene could not be baseline separated and thus are reported as the sum.

Table S8. Concentrations of the target analytes in reference moss samples and oil sands related materils from AOSR (ng/g, dry weight).

	NAP	FLR	PHE	ANT	FLRT	PYR	BaA	CHRY	BbF	BkjF	BaP	IcdP	BghiP	DahA	**$\sum_{13}$PAH**	RET	1-mFLR	1-mPHE	3,6-dPHE	1-mPYR	**∑alkyl-PAH**	**Total PAH**	**∑alkyl-PAH / $\sum_{13}$PAH**
28 (UTK)	5.41	3.37	9.60	0.468	0.880	1.96	0.233	0.521	0.569	0.247	1.37	0.121	0.255	1.85	21.4	4.12	5.49	1.25	0.527	0.245	7.51	34.4	0.351
29 (SEB)	9.52	5.17	13.6	0.468	1.88	3.28	0.284	2.19	0.569	0.247	3.21	0.106	0.658	3.66	35.3	22.2	3.42	2.70	1.14	0.645	7.91	52.7	0.224
30 (EINP)	6.29	2.26	5.65	0.468	1.06	1.86	0.330	0.961	0.569	0.247	1.46	0.122	0.567	1.55	17.1	1.53	4.84	1.09	0.566	0.373	6.87	30.3	0.402
Delayed petcoke1*	631	117	1700	806	517	1510	1540	6310	530	72.0	6360	425	2250	807	22900	6.13	160	770	360	296	1590	25200	0.0694
Delayed petcoke2*	2170	195	3180	860	751	2140	1470	6020	453	139	4670	835	2670	1420	24800	ND	202	644	269	240	1360	28300	0.0548
Fluid petcoke1*	34.5	ND	11.6	ND	11.6	13.6	6.18	9.30	11.0	0.167	ND	ND	ND	ND	63.4	4.26	3.51	3.35	1.25	0.79	8.90	107	0.140
Fluid petcoke2*	147	4.75	21.9	ND	5.08	16.5	2.90	8.21	12.8	0.812	ND	ND	ND	ND	73.0	18.6	5.95	3.87	2.21	1.00	13.0	233	0.178
Exposed bitumen*	23.1	11.9	13.5	21.5	30.7	305	7.45	1200	106	70.3	104	117	211	52.8	2250	782	50.2	63.3	ND	241	355	2630	0.158
Oil sands ore*	37.1	7.10	227	255	37.2	996	168	863	169	76.8	368	204	324	166	3860	399	131	38.3	221	685	1080	4970	0.280
fine tailings*	201	240	2330	180	154	1050	346	1770	276	56.2	345	148	319	81	7300	1120	925	1945	942	607	4420	11900	0.605

*One sample was analyzed. †ND, means no peak could be found. Naphthalene (NAP), Fluorene (FLR), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLRT), Pyrene (PYR), Benz[a]anthracene (BaA), Chrysene (CHRY), Benzo[b]fluoranthene (BbF), Benzo[k+j]fluoranthene (BkjF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IcdP), Benzo[g,h,i]perylene (BghiP), Dibenz[a,h]anthracene (DahA), 1-Methylfluorene (1-mFLR), 1-Methylphenanthrene (1-mPHE), 3,6-Dimethylphenanthrene (3,6-dPHE), 1-Methylpyrene (1-mPYR).

Table S9. CMB source apportionment modeling results (fractions) for moss, and the estimated delayed petcoke concentration in moss (mg/g).

Sampling site number	Source contribution (fractions)									R^2 (>0.80)	χ^2 (<4)	Mass%* (60~140)	Estimated delayed petcoke (mg/g)
	Naturally exposed bitumen	Oil sands ore	Fire ash	Haul road dust	Delayed coke	Stack	Diesel	Fine tailings	Unexplained				
1 N	0.000	0.000	0.254	0.000	0.285	0.268	0.000	0.013	0.179	0.80	3.8	82.1	1.12
2 N	0.000	0.000	0.205	0.000	0.247	0.096	0.008	0.421	0.023	0.88	1.7	97.7	1.06
3 F	0.000	0.000	0.196	0.000	0.087	0.195	0.246	0.000	0.277	0.86	2.3	72.3	0.109
4 F	0.000	0.000	0.194	0.000	0.016	0.408	0.119	0.000	0.262	0.81	1.72	73.8	0.0272
5 F	0.000	0.000	0.250	0.000	0.045	0.281	0.045	0.034	0.345	0.78	1.59	65.5	0.108
6 F	0.000	0.000	0.207	0.000	0.088	0.262	0.064	0.137	0.242	0.79	4.20	75.8	0.240
7 F	0.000	0.000	0.182	0.042	0.294	0.180	0.024	0.014	0.264	0.85	2.05	73.6	0.851
8 F	0.000	0.000	0.241	0.012	0.153	0.134	0.019	0.187	0.253	0.79	3.3	74.7	0.360
9 N	0.000	0.000	0.185	0.000	0.325	0.275	0.000	0.178	0.037	0.87	1.55	96.3	1.28
10 F	0.000	0.000	0.089	0.000	0.271	0.350	0.115	0.023	0.151	0.85	2.85	84.9	0.912
11 F	0.000	0.000	0.168	0.002	0.042	0.279	0.099	0.072	0.339	0.77	4.94	66.1	0.144
12 N	0.000	0.000	0.155	0.000	0.068	0.334	0.043	0.196	0.203	0.84	3.71	79.7	0.290
13 N	0.000	0.000	0.075	0.000	0.069	0.139	0.411	0.000	0.307	0.63	4.76	69.3	0.206
14 F	0.000	0.000	0.105	0.005	0.090	0.196	0.111	0.000	0.493	0.70	5.78	50.7	0.302
15 F	0.000	0.000	0.008	0.000	0.066	0.481	0.339	0.000	0.106	0.81	2.55	89.4	0.297
16 F	0.000	0.000	0.349	0.000	0.237	0.178	0.006	0.000	0.230	0.70	4.12	77.0	0.638
17 N	0.000	0.000	0.087	0.026	0.292	0.304	0.179	0.043	0.068	0.87	3.21	93.2	1.21
18 F	0.000	0.000	0.303	0.000	0.431	0.108	0.000	0.025	0.132	0.83	2.35	86.8	1.64
19 N	0.000	0.000	0.050	0.068	0.746	0.118	0.000	0.018	0.000	0.92	1.19	106.5	8.46
20 F	0.000	0.000	0.117	0.000	0.175	0.291	0.131	0.000	0.286	0.60	10.05	71.4	0.556
21 (ANZ) N	0.000	0.000	0.125	0.013	0.228	0.196	0.123	0.117	0.198	0.85	4.03	80.2	0.906
22(JPH-4) N	0.000	0.000	0.034	0.047	0.139	0.215	0.096	0.249	0.220	0.88	3.45	78.0	0.588
23(MIL) N	0.000	0.029	0.000	0.000	0.949	0.018	0.005	0.000	0.000	0.96	0.36	106.8	16.1
24(McK) N	0.000	0.000	0.038	0.000	0.825	0.000	0.057	0.076	0.004	0.89	1.25	99.6	4.86
Mean	**0.000**	**0.001**	**0.151**	**0.009**	**0.257**	**0.221**	**0.093**	**0.075**	**0.192**	**0.81**	**3.20**	**81.31**	**---**

*When the mass % of a sample is higher than 100, the total source contribution is adjusted to "1" based on the composition. "N" and "F" mean near-field and far-field, respectively.

Table S10. CMB modeling results for peat cores at site 21 (ANZ) and site 22 (JPH-4).

Layer number	Depth (cm)	Source contribution (fractions)									R^2 (>0.80)	χ^2 (<4)	Mass%* (60~140)	∑alkyl-PAH / $\sum_{13}$PAH
		Naturally exposed bitumen	Oil sands ore	Fire ash	Haul road dust	Delayed petcoke	Stack	Diesel	Fine tailings	Unexplained				
ANZ peat core														
1	-2.45	0.000	0.000	0.125	0.045	0.000	0.039	0.27	0.295	0.226	0.81	4.56	79.3	
2	-3.33	0.000	0.000	0.117	0.000	0.013	0.11	0.234	0.207	0.319	0.79	4.08	68.1	
3	-4.18	0.000	0.000	0.109	0.000	0.000	0.123	0.2	0.179	0.389	0.75	4.33	61.1	
4	-5.07	0.000	0.000	0.086	0.000	0.000	0.029	0.152	0.162	0.571	0.71	5.04	43	
5	-5.99	0.000	0.000	0.195	0.000	0.000	0.087	0.175	0.146	0.397	0.75	4.27	60.2	
6	-6.94	0.000	0.000	0.077	0.000	0.000	0.291	0.156	0.081	0.395	0.76	3.94	60.6	
7	-7.86	0.000	0.000	0.077	0.006	0.000	0.243	0.094	0.112	0.468	0.75	4.94	53.2	
8	-8.78	0.000	0.000	0.106	0.000	0.021	0.137	0.138	0.116	0.482	0.70	6.54	51.8	
9	-9.72	0.000	0.000	0.068	0.000	0.000	0.272	0.162	0.115	0.383	0.74	4.51	61.6	
10	-10.62	0.000	0.000	0.12	0.000	0.000	0.191	0.148	0.138	0.403	0.72	4.95	59.7	
JPH-4 peat core														
1	-0.52	0.000	0.000	0.013	0.000	0.369	0.010	0.348	0.261	0.000	0.95	0.8	101.2	0.295
2	-1.50	0.000	0.000	0.084	0.000	0.391	0.000	0.276	0.249	0.000	0.94	0.96	100.6	0.281
3	-2.44	0.000	0.000	0.041	0.000	0.355	0.054	0.298	0.253	0.000	0.93	1.24	100	0.2501
4	-3.37	0.000	0.000	0.069	0.000	0.329	0.053	0.192	0.357	0.000	0.93	1.19	100.2	0.312
5	-4.31	0.000	0.000	0.11	0.000	0.447	0.044	0.106	0.292	0.001	0.91	1.59	99.8	0.252
6	-5.24	0.000	0.000	0.073	0.000	0.326	0.052	0.254	0.263	0.032	0.93	1.29	96.8	0.244
7	-6.18	0.000	0.000	0.124	0.000	0.178	0.055	0.349	0.195	0.099	0.84	3.18	90.1	0.396
8	-7.16	0.000	0.000	0.187	0.000	0.232	0.112	0.27	0.131	0.068	0.87	2.62	93.3	0.276
9	-8.14	0.000	0.000	0.289	0.012	0.162	0.000	0.412	0.000	0.125	0.81	2.97	87.4	0.317
10	-9.08	0.000	0.000	0.246	0.000	0.041	0.067	0.5	0.000	0.146	0.85	2.00	85.4	0.328
11	-10.01	0.000	0.000	0.239	0.000	0.049	0.000	0.486	0.000	0.226	0.78	2.76	77.3	

*When the mass % of a sample is higher than 100, the total source contribution is adjusted to "1" based on the composition. Grey data was used for pearson correlation analysis.

Table S11. CMB modeling results for peat cores at site 23 (MIL) and site 24 (McK).

Layer number	Depth (cm)	Source contribution (fractions)									R^2 (>0.80)	χ^2 (<4)	Mass%* (60~140)	∑alkyl-PAH / $\sum_{13}$PAH
		Naturally exposed bitumen	Oil sands ore	Fire ash	Haul road dust	Delayed petcoke	Stack	Diesel	Fine tailings	Unexplained				
MIL peat core														
1	-0.59	0.000	0.000	0.046	0.000	0.954	0.000	0.000	0.000	0.000	0.91	0.69	104.4	0.153
2	-1.77	0.000	0.000	0.054	0.000	0.798	0.033	0.000	0.115	0.000	0.96	0.47	104	0.257
3	-2.95	0.000	0.000	0.050	0.000	0.777	0.025	0.000	0.147	0.000	0.97	0.4	103.8	0.299
4	-4.11	0.000	0.000	0.058	0.000	0.672	0.033	0.000	0.237	0.000	0.96	0.51	102.5	0.640
5	-5.28	0.000	0.073	0.000	0.041	0.822	0.035	0.008	0.022	0.000	0.96	0.63	103.3	0.298
6	-6.40	0.000	0.000	0.009	0.000	0.691	0.038	0.003	0.260	0.000	0.96	0.59	103.4	0.408
7	-7.48	0.000	0.000	0.000	0.000	0.738	0.016	0.000	0.246	0.000	0.94	0.61	100.4	0.250
8	-8.57	0.000	0.000	0.033	0.000	0.641	0.026	0.000	0.301	0.000	0.95	0.59	100.7	0.242
9	-9.69	0.000	0.000	0.059	0.000	0.520	0.045	0.000	0.346	0.03	0.92	1.06	97	0.251
10	-10.82	0.000	0.000	0.081	0.000	0.472	0.074	0.000	0.309	0.064	0.89	1.55	93.6	0.278
11	-11.95	0.000	0.000	0.049	0.000	0.438	0.201	0.000	0.261	0.051	0.84	2.37	94.8	0.296
McK peat core														
1	-0.56	0.000	0.000	0.033	0.000	0.764	0.000	0.055	0.133	0.015	0.89	1.41	98.5	0.201
2	-1.68	0.000	0.000	0.054	0.000	0.782	0.020	0.021	0.116	0.007	0.88	1.73	99.3	0.182
3	-2.79	0.000	0.000	0.083	0.000	0.719	0.023	0.020	0.126	0.029	0.86	2.15	97	0.227
4	-3.92	0.000	0.000	0.101	0.000	0.579	0.047	0.011	0.203	0.059	0.84	2.73	94	0.252
5	-5.05	0.000	0.000	0.129	0.000	0.623	0.029	0.000	0.176	0.043	0.86	1.96	95.7	0.292
6	-6.17	0.000	0.000	0.152	0.000	0.527	0.030	0.017	0.217	0.057	0.84	2.67	94.3	0.274
7	-7.30	0.000	0.000	0.162	0.000	0.096	0.086	0.030	0.308	0.318	0.66	7.73	68.2	
8	-8.41	0.000	0.000	0.000	0.000	0.212	0.556	0.000	0.000	0.232	0.45	6.13	76.8	
9	-9.52	0.000	0.000	0.000	0.000	0.266	0.290	0.050	0.023	0.371	0.49	7.88	62.8	
10	-10.63	0.000	0.000	0.000	0.000	0.236	0.382	0.018	0.000	0.364	0.48	6.73	63.6	

*When the mass % of a sample is higher than 100, the total source contribution is adjusted to "1" based on the composition. Grey data was used for pearson correlation analysis.

Table S12. Metal concentration in delayed petcoke sample and estimated delayed petcoke contribution to metal in moss reported by Shotyk et al. [9]

	∑13 PAHs	V	Ni	Mo	Ag	Cd	Sb	Ba	Tl	Pb	Th
Delayed petcoke 1 (μg/g)	22.9	1200	378	47.8	0.0766	0.0363	0.0682	108	0.0581	8.01	2.85
					Delayed petcoke contribution (%)						
1	28.5	25.8	20.6	13.6	0.402	0.0831	0.141	0.409	0.249	0.917	0.833
2	24.7	25.4	20.1	17.3	0.402	0.150	0.133	0.360	0.241	0.861	0.732
3	8.70	11.2	6.97	3.86	0.0640	0.0198	0.0507	0.112	0.0603	0.255	0.323
4	1.60	1.97	1.26	0.915	0.0137	0.0042	0.0096	0.0151	0.0109	0.0437	0.0373
5	4.50	6.46	3.86	2.67	0.0405	0.0173	0.0336	0.0653	0.0521	0.183	0.202
6	8.80	16.3	11.5	8.48	0.104	0.0373	0.0962	0.186	0.120	0.462	0.519
7	29.4	34.9	24.7	17.1	0.375	0.178	0.217	0.491	0.235	0.930	0.748
8	15.3	19.2	13.4	11.0	0.230	0.0799	0.115	0.251	0.147	0.509	0.480
9	32.5	35.2	25.3	12.4	0.515	0.199	0.256	0.528	0.294	1.12	0.991
10	27.1	32.6	24.5	15.5	0.395	0.105	0.188	0.421	0.243	0.836	0.752
11	4.20	6.97	4.81	2.73	0.0464	0.0276	0.0447	0.0838	0.0652	0.214	0.216
12	6.80	4.92	3.78	2.56	0.0836	0.0385	0.0414	0.0680	0.0370	0.155	0.179
13	6.90	6.51	5.08	3.62	0.0881	0.0350	0.0404	0.0818	0.0501	0.193	0.169
14	9.00	28.6	11.5	7.30	0.137	0.0283	0.131	0.290	0.124	0.860	1.12
15	6.60	16.1	10.2	5.86	0.134	0.0514	0.0620	0.229	0.179	0.537	0.640
16	23.7	42.5	27.2	15.0	0.321	0.118	0.207	0.581	0.368	1.13	1.29
17	29.2	39.3	26.1	17.1	0.369	0.219	0.334	0.642	0.368	1.25	1.24
18	43.1	48.0	42.2	30.6	0.852	0.232	0.391	1.07	0.474	1.87	1.72
19	74.6	138	108	74.6	2.49	1.30	1.41	3.27	1.78	6.49	5.72
20	17.5	39.9	28.4	16.2	0.334	0.132	0.223	0.682	0.266	1.00	1.17
21 (ANZ)	22.8	64.5	29. 5	25.0	0.301	0.167	0.191	0.736	0.639	1.56	2.69
22(JPH-4)	13.9	15.8	10.1	8.68	0.160	0.0831	0.102	0.156	0.119	0.473	0.418
Max	**74.6**	**138**	**108**	**74.6**	**2.49**	**1.30**	**1.41**	**3.27**	**1.78**	**6.49**	**5.72**
Min	**1.60**	**1.97**	**1.26**	**0.915**	**0.0137**	**0.0042**	**0.0096**	**0.0151**	**0.0109**	**0.0437**	**0.0373**
Mean	**20.0**	**30.0**	**20.9**	**14.2**	**0.357**	**0.150**	**0.201**	**0.488**	**0.278**	**0.993**	**1.01**
Median	**16.4**	**25.6**	**16.7**	**11.7**	**0.266**	**0.0831**	**0.132**	**0.325**	**0.207**	**0.848**	**0.740**

Table S13. Particulate, dissolved, and total PAHs and retene deposition in snow (μg/m^2).

Sampling site number	NAP	FLR	PHE	ANT	FLRT	PYR	BaA	CHRY	BbF	BkjF	BaP	IcdP	BghiP	DahA	$\sum_{13}$ PAHs	RET	1-mFLR	1-mPHE	3,6-dPHE	1-mPYR	∑alkyl-PAH	Total PAH	∑alkyl-PAH / $\sum_{13}$PAH
Snow particle																							
21 (ANZ)	1.78	0.062	0.742	0.218	0.628	1.04	0.235	0.819	0.162	0.065	0.100	0.162	0.552	0.096	4.88	0.185	5.03	0.171	0.059	0.071	5.33	12.0	1.09
22 (JPH-4)	3.87	0.374	2.67	0.743	0.562	2.39	0.833	6.45	0.837	0.196	0.652	0.595	1.46	0.469	18.2	1.48	2.24	1.26	0.266	0.479	4.24	26.3	0.233
23 (MIL)	4.52	1.03	9.39	4.36	1.62	9.29	5.89	23.0	3.18	0.343	2.94	2.40	7.61	4.91	76.0	0.765	4.85	3.70	1.93	2.23	12.7	93.2	0.167
24 (McK)	2.18	0.271	3.08	0.812	0.575	2.17	1.29	5.56	0.682	0.146	0.205	0.498	1.84	0.505	17.6	1.13	4.96	1.35	0.625	0.410	7.34	27.1	0.416
25 (McM)	2.33	0.112	0.627	0.211	0.276	0.845	0.323	0.864	0.166	0.060	0.126	0.175	0.430	0.127	4.34	0.358	2.38	0.244	0.111	0.118	2.85	9.52	0.657
Snow water																							
21 (ANZ)	12.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.036	ND	ND	0.036	ND	ND	ND	0.026	0.007	0.033	12.7	0.916
22 (JPH-4)	11.1	ND	ND	ND	ND	ND	0.141	0.115	ND	ND	ND	0.040	0.027	ND	0.323	ND	ND	0.060	0.013	0.011	0.084	11.5	0.260
23 (MIL)	11.8	ND	ND	ND	ND	ND	0.194	0.396	ND	ND	0.129	0.065	0.141	ND	0.924	ND	ND	0.097	0.061	0.042	0.200	12.9	0.216
24 (McK)	8.17	ND	ND	ND	ND	ND	ND	0.106	ND	ND	ND	0.048	0.038	ND	0.192	ND	ND	0.064	0.020	0.018	0.102	8.46	0.533
25 (McM)	7.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.025	ND	0.025	ND	ND	ND	0.024	ND	0.024	7.55	0.948
Total snow particle and water																							
21 (ANZ)	14.3	0.062	0.742	0.218	0.628	1.04	0.235	0.819	0.162	0.065	0.100	0.198	0.552	0.096	4.92	0.185	5.03	0.171	0.085	0.078	5.36	24.6	1.09
22 (JPH-4)	15.0	0.374	2.667	0.743	0.562	2.39	0.973	6.56	0.837	0.196	0.652	0.635	1.48	0.469	18.5	1.48	2.24	1.32	0.279	0.491	4.33	37.8	0.233
23 (MIL)	16.3	1.03	9.39	4.36	1.62	9.29	6.08	23.4	3.18	0.343	3.067	2.46	7.75	4.91	76.9	0.765	4.85	3.79	1.99	2.28	12.9	106	0.168
24 (McK)	10.4	0.271	3.08	0.812	0.575	2.17	1.29	5.67	0.682	0.146	0.205	0.546	1.88	0.505	17.8	1.13	4.96	1.41	0.645	0.428	7.44	35.6	0.417
25 (McM)	9.83	0.112	0.627	0.211	0.276	0.845	0.323	0.864	0.166	0.060	0.126	0.175	0.455	0.127	4.37	0.358	2.38	0.244	0.135	0.118	2.88	17.1	0.658

†ND, means no peak could be found. ‡Ratio here means ∑4 alkyl PAHs/∑13 PAHs. Naphthalene (NAP), Fluorene (FLR), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLRT), Pyrene (PYR), Benz[a]anthracene (BaA), Chrysene (CHRY), Benzo[b]fluoranthene (BbF), Benzo[k+j]fluoranthene (BkjF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IcdP), Benzo[g,h,i]perylene (BghiP), Dibenz[a,h]anthracene (DahA), 1-Methylfluorene (1-mFLR), 1-Methylphenanthrene (1-mPHE), 3,6-Dimethylphenanthrene (3,6-dPHE), 1-Methylpyrene (1-mPYR).

Figure S1. Snow core collection with sampler (A), petcoke-like chunks (B and C) and small black particles (D) in snow along the railway near to Anzac (site 21).

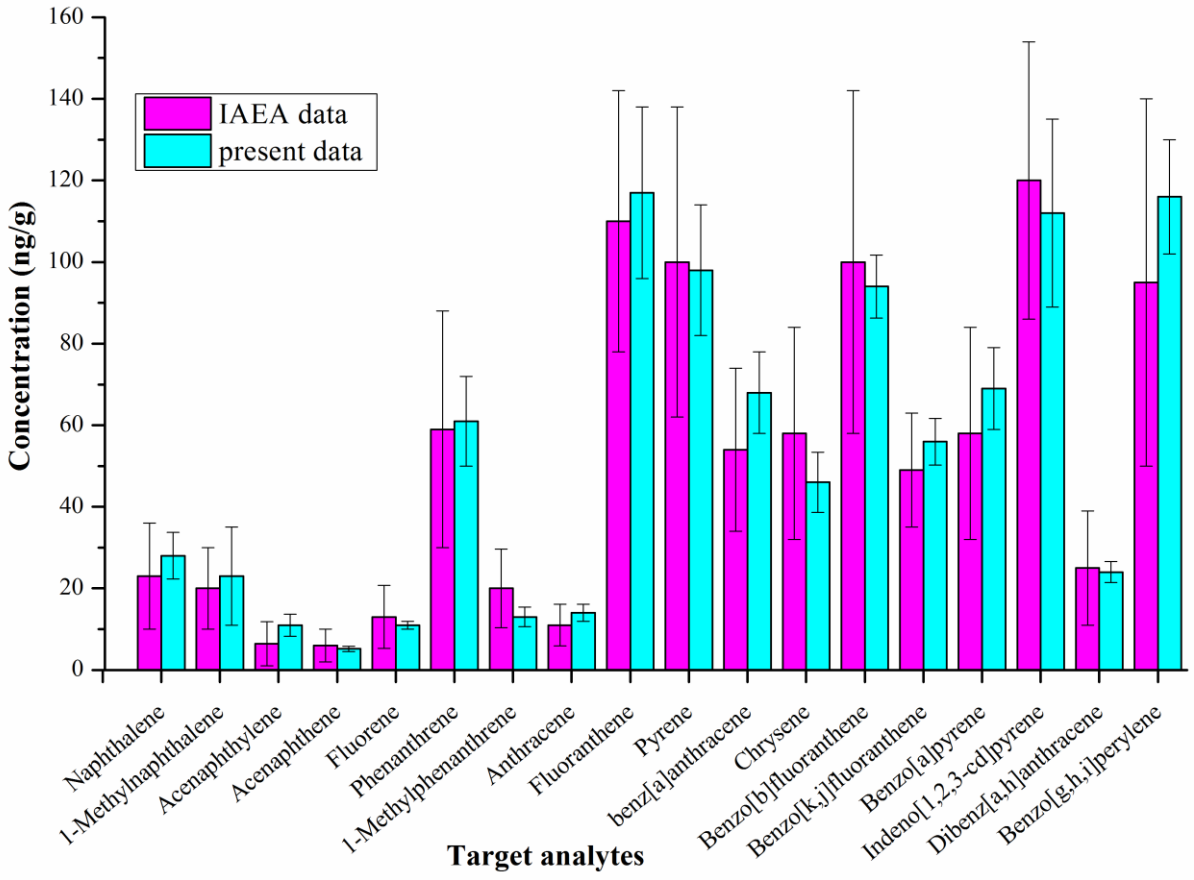

Figure S2. Comparison of mean measured (n=8) and nominal PAHs concentrations in reference sediment IAEA-159. Error bars represent standard deviation. *Benzo[k]fluoranthene and Benzo[j]fluoranthene could not be baseline separated in the present study and thus are reported as the sum, and only concentration of benzo[k]fluoranthenethe in the reference sediment are provided by the distributor.

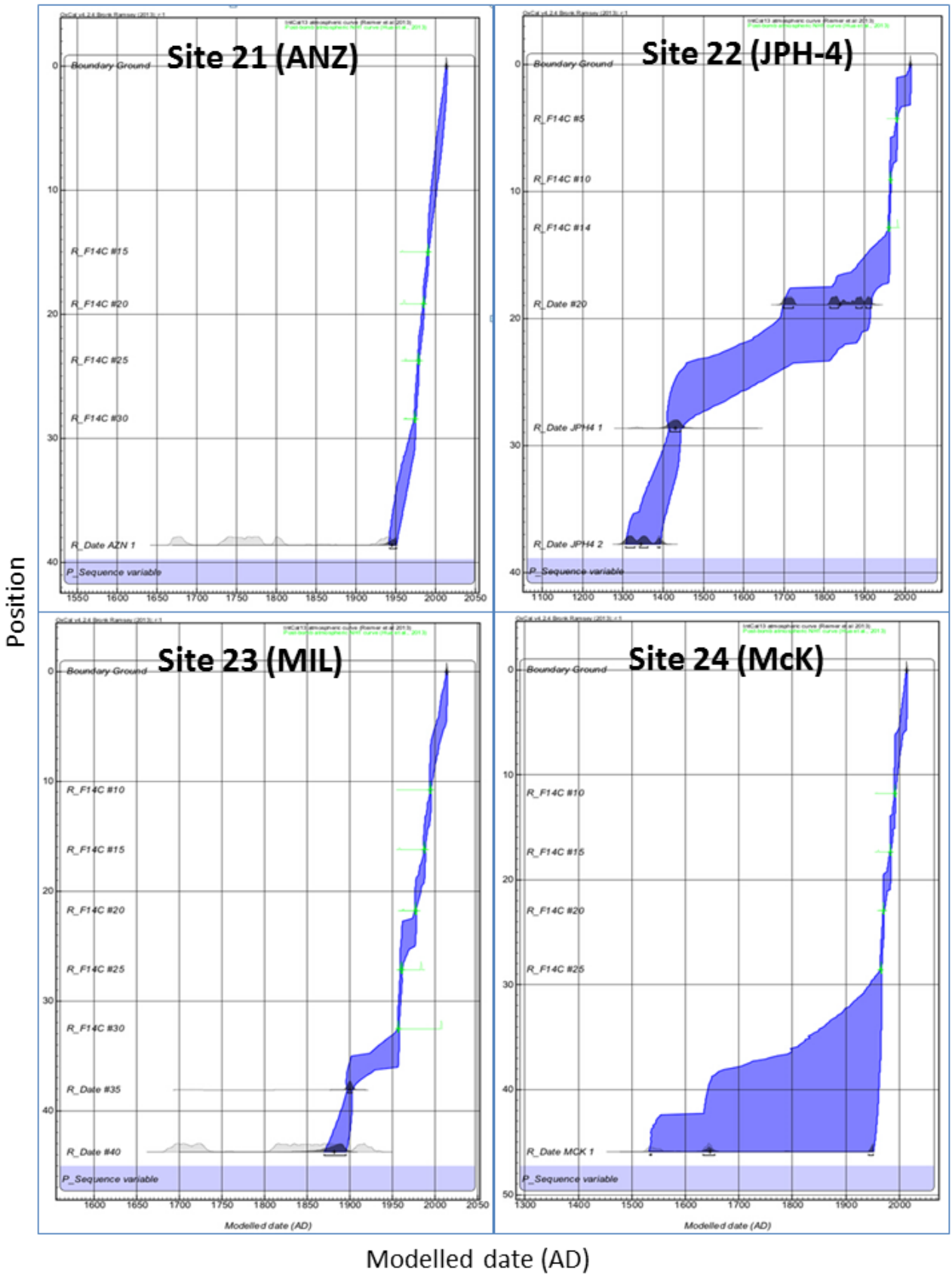

Figure S3. ^{14}C age-depth models for the four peat cores produced using the P_Sequence function of Oxcal v4.2 with 1 year resolution. Individual ^{14}C dates are labelled; blue areas show the 68.2% age range.

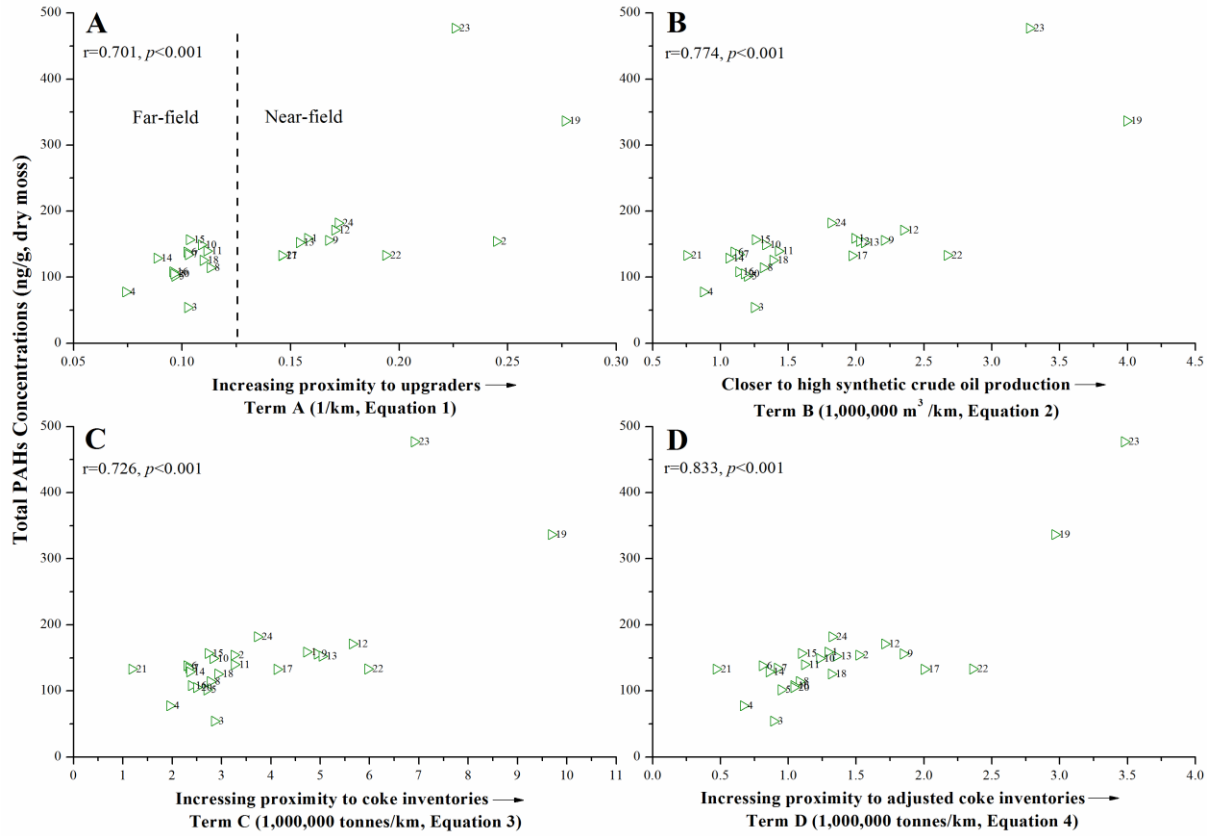

Figure S4. Pearson correlations among total PAHs in moss at each site and various terms related to source proximity.

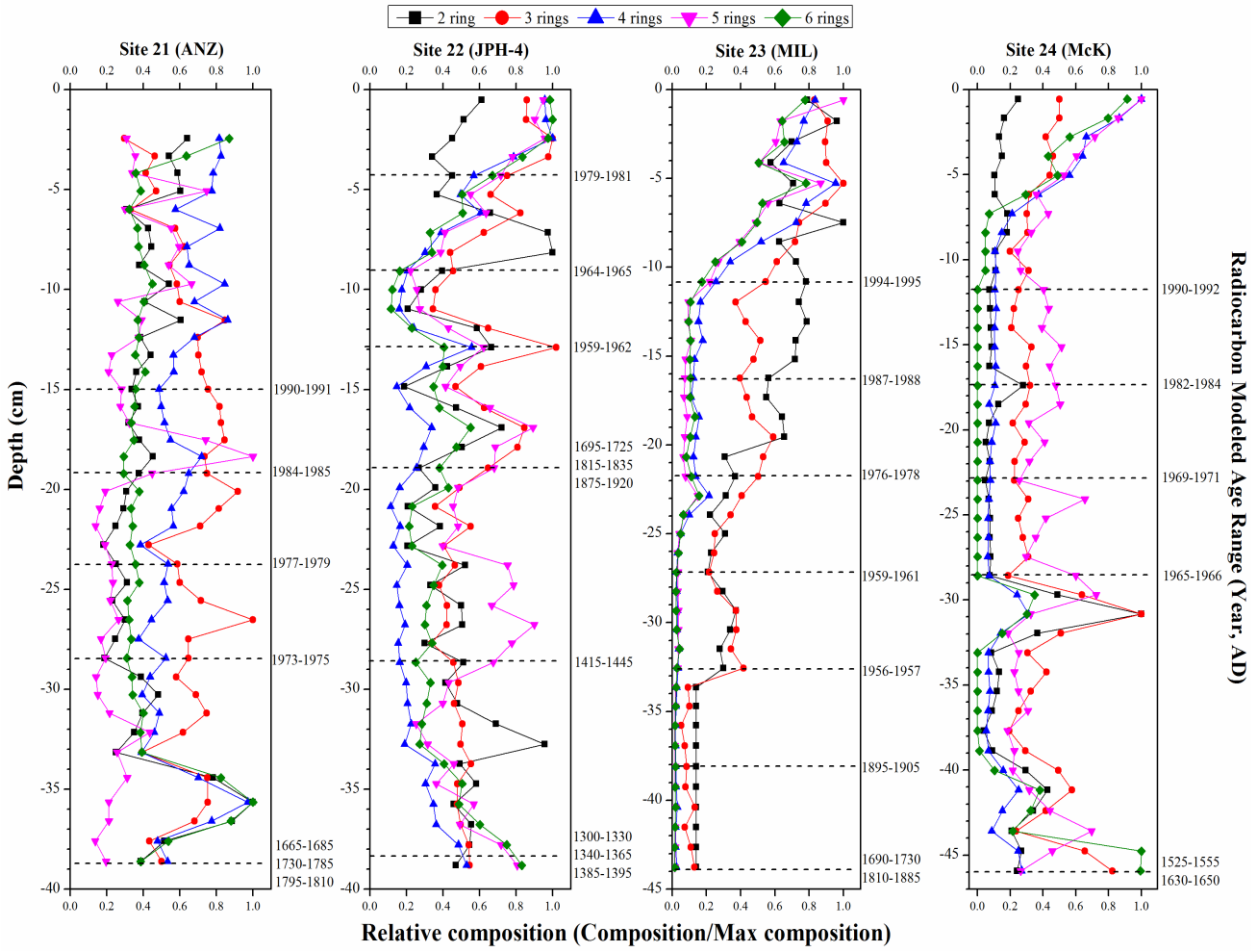

Figure S5. Relative composition of parent PAHs, grouped by number of rings, in the four peat cores.

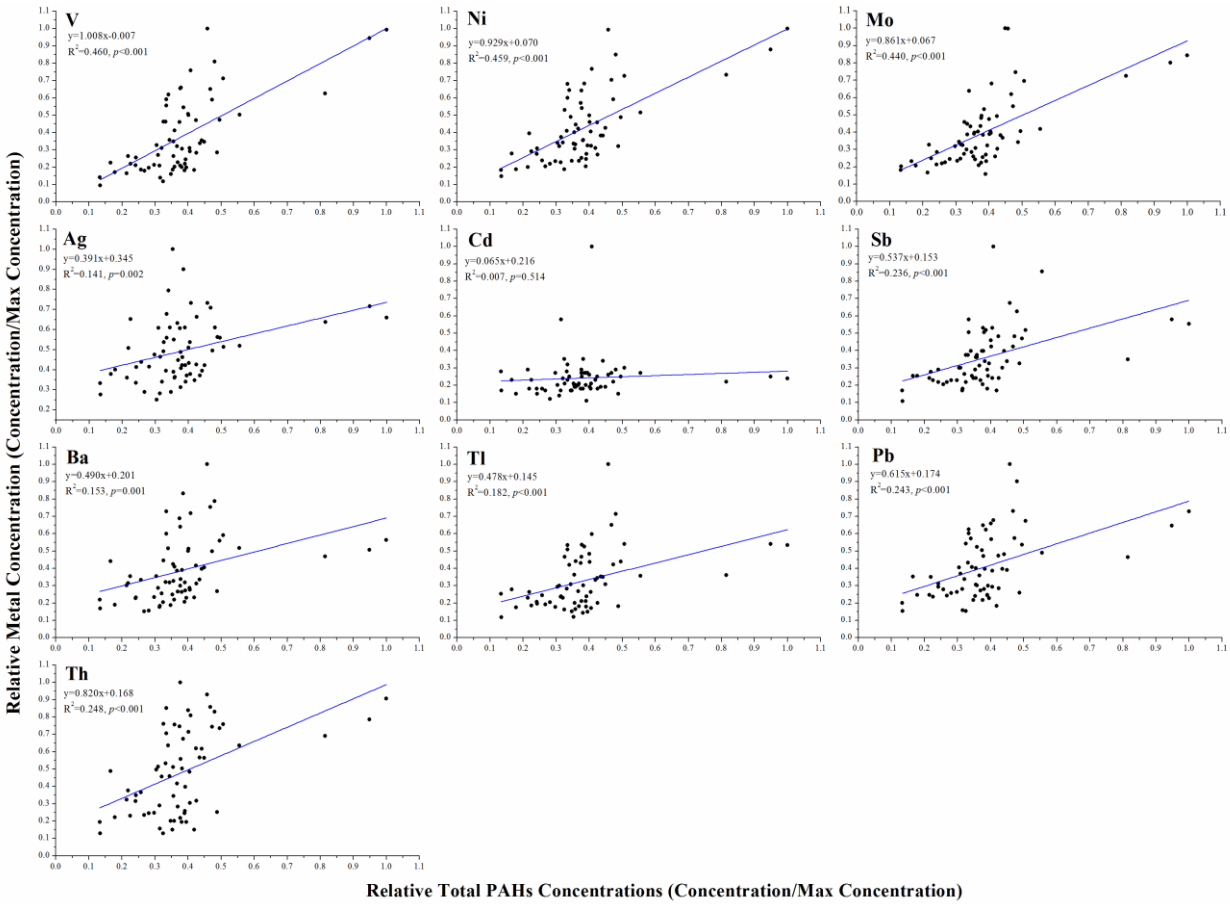

Figure S6. Linear regression of various metals and total PAHs in moss samples. All concentrations have been normalized to the maximum concentration within each dataset (e.g. maximum concentrations are always 1.0).

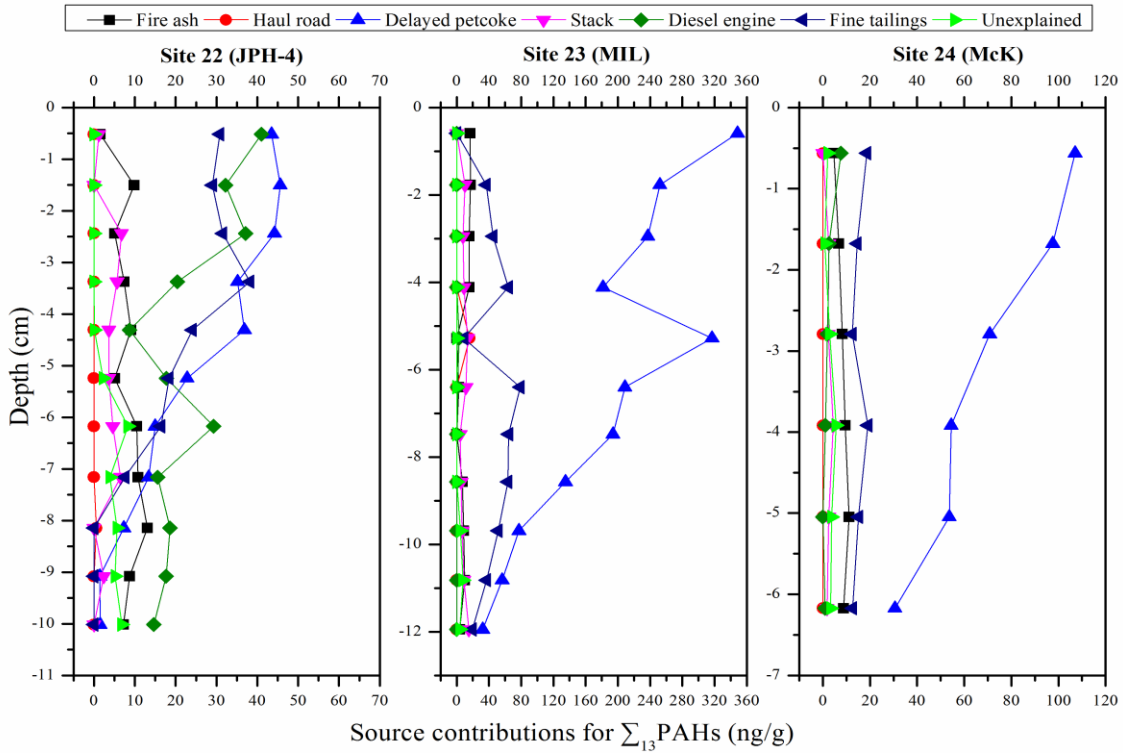

Figure S7. Source contribution to $\sum_{13}$PAHs at various depths in peat cores based on CMB modeling. The fit of the CMB model was not acceptable for any layer except the very top layer of peat (Table S6), thus data for site 21 are not plotted.

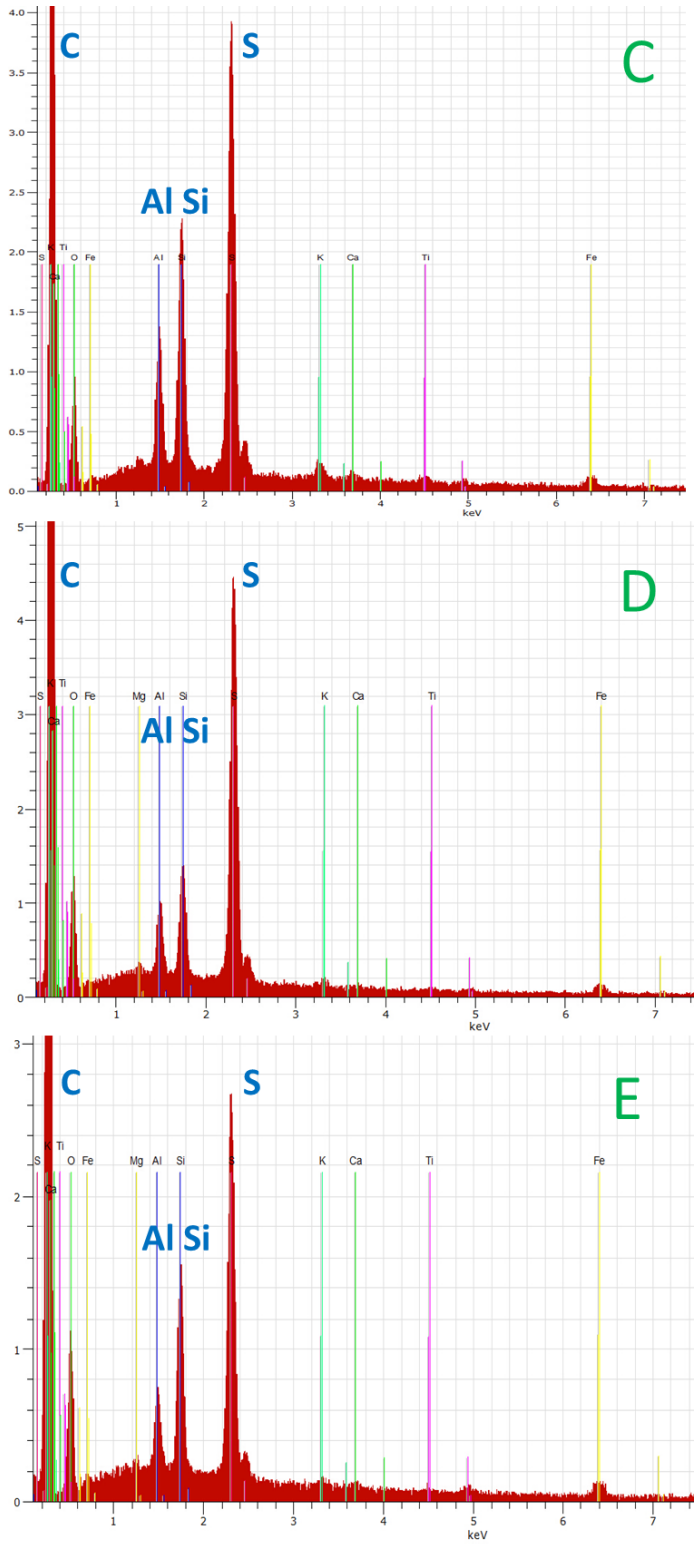

Figure S8. EDS spectra of petcoke-like particles in snow from site 23 (MIL Bog). Points C, D, E are shown in SEM images (Figure 4).

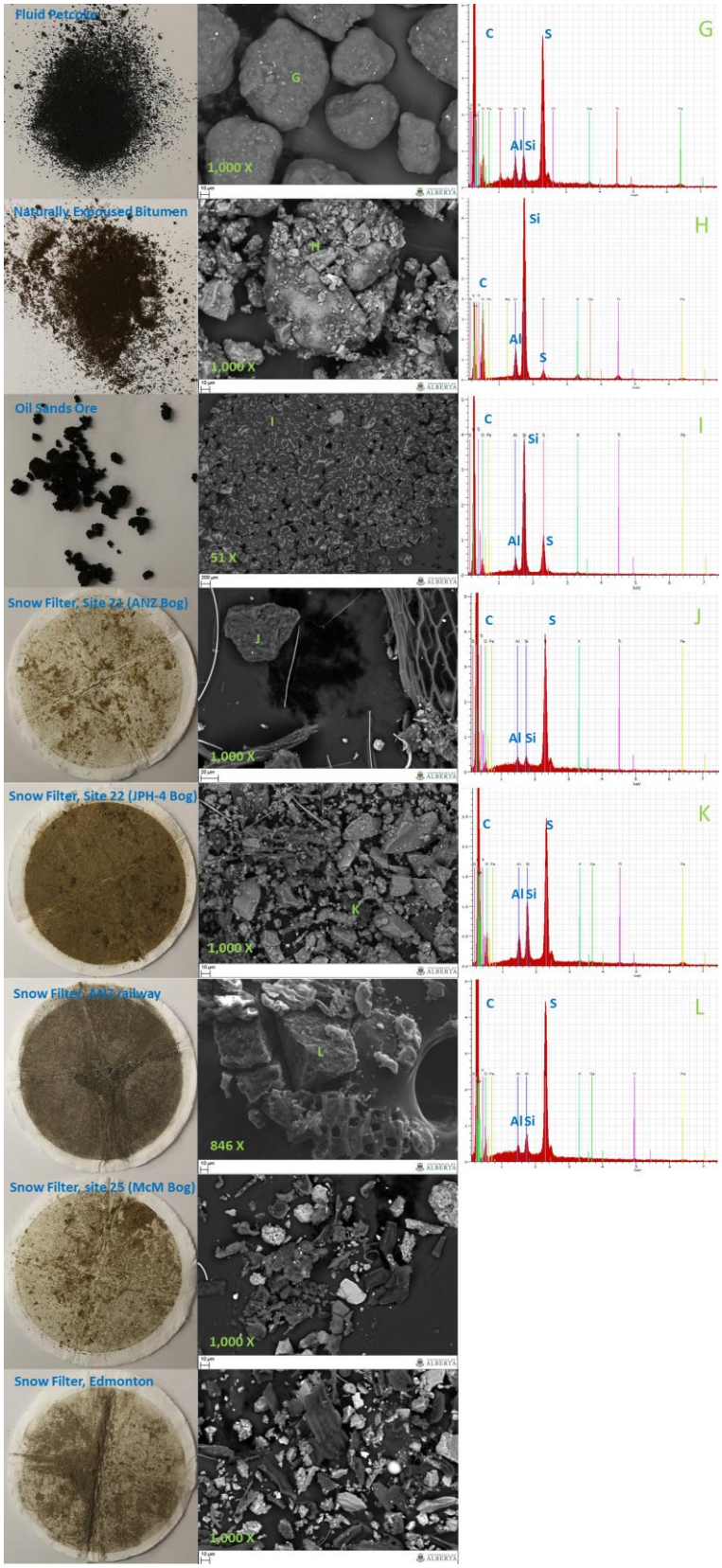

Figure S9. SEM images and associated EDS spectra of authentic fluid petcoke, naturally exposed bitumen, oil sands ore and snow particles. The letters in the SEM images indicate points at which EDS spectra were recorded. No petcoke-like particles could be seen in snow filters from site 25 (McM Bog) or from urban snow in Edmonton, thus no associated EDS spectra are shown.

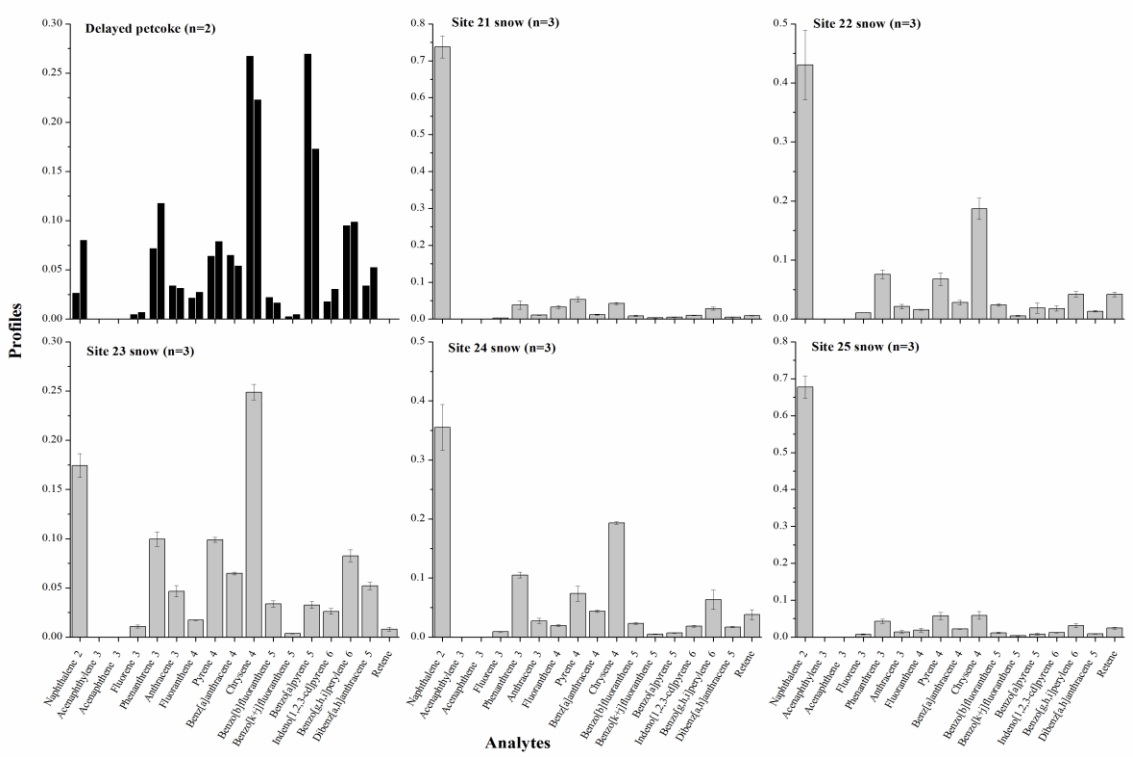

Figure S10. Relative PAH (ring number shown) and retene composition in delayed petcoke and snow samples (collected 2015) from the AOSR.

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