Supplementary Materials

Fate and Occurrence of Polycyclic Aromatic Hydrocarbons and their Derivatives in Water and Sediment from Songhua River, Northeast China

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Chemicals and Reagents

All the solvents utilized in the experiments were high-performance liquid chroma- tography (HPLC)-grade quality. Dichloromethane (DCM), methanol (MeOH) and toluene were purchased from Fisher Scientific (Fair lawn, New Jersey, USA). Pure (>18 MΩ-cm R) reagent water was prepared by a Milli-Q system (Mil- lipore, Billerica, MA).

Each of the PAHs mixture standards was purchased from AccuStandard (New Ha- ven, CT, USA). The 98% pure deuterium-labeled 16 PAHs mixture standards was pur- chased from AccuStandard. 2-Methylnaphthalene-d10, 1-Me- thylnaphthalene-d10, 9- Methylanthracene-d12, 1-Nitronaphthalene-d7 and 9-Ni- troanthracene-d9 were pur- chased from Chiron (Norway).

Table S1. Sampling sites information selected to collect sediment and water samples.

Sediment and water sites	Descriptions	Longitude	Latitude	Sizes	Population ($\times 10^4$)	Locations
S1 and W1	the downstream of Jilin City	126	44.0	Medium city	430 2012	Jilin (Second Songhua River)
S2 and W2	the downstream of Songyuan City	124	45.1	Medium city	278 2015	Jilin (Second Songhua River)
S3 and W3	the downstream of Da'an City	124	45.5	Small city	43 2013	Jilin (Nen River)
S4 and W4	the downstream of ZhaoyuanCounty	124	45.4	Small city	47.5 2013	Heilongjiang (Songhua River)
S5 and W5	the upstream of Qiqihaer City	124	47.5	Medium city	571 2010	Heilongjiang (Nen River)
S6 and W6	the downstream of Harbin City	127	46	Big city	961 2015	Heilongjiang (Songhua River)
S7 and W7	the downstream of Tonghe County	128	45.8	Small city	23.9 2009	Heilongjiang (Songhua River)
S8 and W8	the downstream of Yilan County	129	46.3	Small city	39 2015	Heilongjiang (Songhua River)
S9 and W9	the upstream of Jiamusi City	130	46.8	Medium city	255 2010	Heilongjiang (Songhua River)
S10 and W10	the middle of Tangwang River	129	46.6	Small city	272015	Heilongjiang (Songhua River)
S11 and W11	the middle of Mudan River	129	45.6	length is 1705,	-	the second largest tributary of Songhua River
S12 and W12	the upper stream of Mudanjiang City	129	44.6	Medium city	278 2012	Heilongjiang (Mudan River)
S13 and W13	The middle of Lalin River	126	45.1	length is 448 km	-	feeds into Songhua River

S14 and W14	The end of Heilong River	126	45.9	length is 523 km	-	Heilongjiang (Heilong River)
S15 and W15	The middle of Hulan River	126	46.2	length is 523 km	-	feeds into Songhua River at Hulan District
S16 and W16	Ma Yan River	128	45.8	length is 341 km	-	tributary in the right of Song-hua River

Table S2. GC-MS/MS detection parameters of target PAHs, Me-PAHs and NPAHs including the optimized.

Analytes	Retention Time (min)	Transition 1 (m/z)	CE 1 (eV)	Transition 2 (m/z)	CE 2 (eV)
Naphthalene	5.077	128→102	20	128→127	20
Naphthalene-D8	5.020	136→108	10	136→84	15
Acenaphthylene	7.142	152→150	25	152→151	25
Acenaphthylene-D8	7.098	160→158	25	160→132	30
Acenaphthene	7.399	153→152	25	153→151	25
Acenaphthene-D10	7.328	162→160	30	162→158	30
Fluorene	8.213	166→165	25	165→163	30
Fluorene-D10	8.134	176→174	20	176→172	40
Phenanthrene	10.630	178→176	25	178→152	25
Phenanthrene-D10	10.508	188→160	30	188→184	40
Anthracene	10.793	178→176	25	178→152	25
Fluoranthene	15.356	202→200	35	202→201	25
Fluoranthene-D10	15.261	212→208	40	212→210	30
Pyrene	16.053	202→200	35	202→201	25
Pyrene-D10	15.965	212→208	40	212→210	40
Benz(a)anthracene	19.670	228→226	30	228→202	30
Benz(a)anthracene-D12	19.589	240→236	40	240→212	40
Chrysene	19.779	228→226	30	228→202	30
Chrysene-D12	19.681	240→236	40	240→212	30
Benzo[b]fluoranthene	22.325	252→250	30	252→226	25
Benzo[b]fluoranthene-D12	22.249	264→260	40	264→236	40
Benzo[k]fluoranthene	22.389	252→250	30	252→226	25
Benzo[k]Fluoranthene-D12	22.312	264→260	40	264→236	40
Benzo[a]pyrene	22.996	252→250	30	252→226	25
Benzop[a]pyrene-D12	22.921	264→260	40	264→236	40
Indeno[1,2,3-cd]pyrene	25.331	276→274	45	276→272	50
Indeno[1,2,3-cd]pyrene-D12	25.253	288→284	40	288→286	40
Dibenz(a,h)anthracene	25.410	278→274	55	278→276	50
Dibenzo[a,h]anthracene-D14	25.309	292→288	40	292→290	30
Benzo[g,h,i]perylene	25.914	276→274	45	276→272	50
Benzo[g,h,i]perylene-D12	25.820	288→284	40	288→286	30
Me-PAHs					
2-Methylnaphthalene	9.245	141→115	20	142→141	20
2-Methylnaphthalene-d10	9.050	150→122	30	152→122	35
1-Methylnaphthalene	9.548	141→115	20	142→141	20
1-Methylnaphthalene-d10	9.354	152→150	20	150→122	20
2,6-Dimethylnaphthalene	11.156	156→141	20	156→115	40
2,7-Dimethylnaphthalene	11.165	156→141	15	141→115	20
1,3-Dimethylnaphthalene	11.410	141→115	20	156→141	20
1,6-Dimethylnaphthalene	11.459	156→141	20	141→115	20
1,4-Dimethylnaphthalene	11.732	141→115	20	156→141	20
1,5-Dimethylnaphthalene	11.783	141→115	20	156→141	20
1,2-Dimethylnaphthalene	11.982	141→115	25	156→141	15
2-Methylphenanthrene	19.414	192→191	20	191→189	30
2-Methylanthracene	19.680	192→191	20	192→189	40
1-Methylanthracene	19.964	192→191	20	192→189	40

1-Methylphenanthrene	20.029	192→191	20	191→189	30
9-Methylanthracene	21.015	192→191	20	191→189	30
9-Methylanthracene-d12	20.753	204→202	25	202→198	30
3,6-Dimethylphenanthrene	22.588	206→191	20	206→189	45
2,3-Dimethylanthracene	25.113	206→191	20	206→189	45
9,10-Dimethylanthracene	27.022	206→191	20	191→189	30
9-Methyl-9-phenylfluorene	27.197	241→239	35	256→241	15
2-Methylfluoranthene	28.001	216→215	25	215→213	40
1-Methylpyrene	29.192	216→215	25	215→189	30
1,2-Methylbenz[a]anthracene	31.975	242→241	20	242→239	50
7,9-Methylbenz[a]anthracene	32.038	242→241	20	242→239	45
4,6-Methylbenz[a]anthracene	32.100	242→241	20	242→239	45
3,5-Methylbenz[a]anthracene	32.218	242→241	20	242→239	50
10-Methylbenz[a]anthracene	32.453	242→241	20	242→239	45
5,8-Dimethylbenzo[c]phenanthrene	32.751	256→241	20	256→239	50
6,8-Dimethylbenz[a]anthracene	32.848	256→239	45	256→241	20
3,9Dimethylbenz[a]anthracene	32.891	256→239	50	256→255	25
7,12-Dimethylbenz(a)anthracene	33.305	256→241	20	256→239	50
3-Methylcholanthrene	34.467	268→252	40	268→253	20
8,9-Methylbenzo[a]pyrene	34.512	266→265	20	266→263	50
7,10-Methylbenzo[a]pyrene	34.693	266→265	20	266→263	50
7,10-Dimethylbenzo[a]pyrene	35.722	280→265	20	280→264	35
NPAHs					
1-Nitronaphthalene	14.293	127→77	15	173→115	20
1-Nitronaphthalene-D7	14.254	180→122	35	134→82	20
2-Nitronaphthalene	14.881	173→115	10	127→77	20
2-Nitrobiphenyl	15.581	152→151	20	182→154	15
4-Nitrobiphenyl	18.356	199→169	10	199→141	20
5-Nitroacenaphthene	22.659	199→169	10	152→151	25
2,2'-Dinitrobiphenyl	24.842	198→115	20	168→139	25
9-Nitroanthracene	27.170	223→193	15	223→165	35
9-Nitroanthracene-D9	27.121	232→174	35	232→202	15
9-Nitrophenanthrene	28.492	177→176	15	223→165	25
2-Nitrodibenzothiophene	28.882	183→139	20	229→183	20
3-Nitrophenanthrene	29.133	223→165	15	223→177	20
2-Nitroanthracene	29.699	223→177	20	177→176	15
9,10-Dinitroanthracene	30.138	268→55	10	176→150	20

Table S3. Concentrations of target compounds in water (ng/L) and sediment (ng/g) samples from the Songhua River, North China.

PAHs	**Water (ng/L)**					**Sediment (ng/g)**			
	Min	Max	Mean	Median		Min	Max	Mean	Median
W1	BDL	71.2	11.4	3.86	S1	0.43	34.3	6.64	2.64
W2	BDL	183	25.8	8.96	S2	0.26	97.7	18.6	6.16
W3	BDL	56.7	12.2	5.11	S3	0.74	36.3	9.88	4.36
W4	2.21	149	27.1	11.8	S4	0.22	43.1	8.66	1.96
W5	BDL	84.5	11.1	2.90	S5	3.56	67.5	27.6	22.0
W6	0.55	188	25.4	5.93	S6	0.14	15.8	2.98	1.46
W7	BDL	107	16.8	6.7	S7	3.03	42.8	20.4	20.8
W8	BDL	144	17.2	4.72	S8	0.47	31.7	6.63	2.16
W9	1.39	88.6	17.5	8.40	S9	1.02	63.4	15.2	5.71
W10	BDL	72.1	12.7	4.33	S10	4.27	382	122	119
W11	BDL	151	29.0	12.1	S11	0.97	40.2	13.0	8.16
W12	BDL	114	16.0	4.18	S12	0.23	30.6	5.9	1.30
W13	BDL	69.0	16.6	5.58	S13	0.32	31.3	6.08	2.40
W14	1.26	126	22.3	7.16	S14	0.55	14.6	4.6	3.15
W15	BDL	67.7	10.7	3.88	S15	0.26	22.0	4.67	1.29
W16	BDL	90.1	13.1	3.66	S16	0.27	52.4	9.50	4.53
Me-PAHs	Min	Max	Mean	Median		Min	Max	Mean	Median
W1	BDL	35.5	6.17	2.45	S1	BDL	15.6	1.73	0.13
W2	BDL	31.9	2.82	0.09	S2	BDL	4.16	0.14	BDL

W3	BDL	32.1	2.83	0.10	S3	BDL	31.7	10.9	9.00
W4	BDL	23.2	2.98	0.35	S4	BDL	16.4	2.98	1.93
W5	BDL	26.8	3.50	0.69	S5	BDL	9.71	1.28	0.52
W6	BDL	40.1	6.58	2.07	S6	BDL	9.68	1.05	0.15
W7	BDL	28.7	4.29	0.38	S7	BDL	13.8	2.63	1.28
W8	BDL	32.7	3.64	0.18	S8	BDL	9.86	1.89	1.14
W9	BDL	37.3	2.53	0.30	S9	BDL	6.09	0.87	0.35
W10	BDL	46.5	8.17	2.99	S10	BDL	7.83	1.76	1.09
W11	BDL	49.6	7.72	3.99	S11	BDL	9.67	1.60	0.39
W12	BDL	42.0	4.82	0.64	S12	BDL	13.8	1.90	0.36
W13	BDL	44.6	5.14	0.57	S13	BDL	9.62	0.98	0.04
W14	BDL	36.1	5.89	2.51	S14	BDL	13.9	2.82	2.27
W15	BDL	22.0	3.55	0.27	S15	BDL	62.5	7.39	4.62
W16	BDL	40.1	4.45	0.08	S16	BDL	11.9	1.66	0.55
NPAHs	Min	Max	Mean	Median		Min	Max	Mean	Median
W1	BDL	8.05	2.09	0.32	S1	BDL	2.62	0.49	0.07
W2	BDL	4.05	0.66	0.21	S2	BDL	0.52	0.04	BDL
W3	BDL	4.20	0.58	0.06	S3	BDL	4.02	1.22	0.24
W4	BDL	3.19	0.68	0.26	S4	BDL	4.80	1.06	0.19
W5	BDL	9.05	1.13	0.17	S5	BDL	0.63	0.14	0.01
W6	BDL	9.12	1.76	0.60	S6	BDL	2.07	0.29	0.01
W7	BDL	11.5	3.42	0.85	S7	BDL	1.63	0.22	0.04
W8	BDL	1.76	0.45	0.25	S8	BDL	4.08	0.85	0.35
W9	BDL	3.72	0.62	0.05	S9	BDL	4.34	0.61	0.07
W10	BDL	6.36	0.79	0.15	S10	BDL	2.34	0.66	0.31
W11	BDL	2.50	0.44	0.14	S11	BDL	1.93	0.44	0.10
W12	BDL	13.2	2.44	0.40	S12	BDL	1.77	0.42	0.10
W13	BDL	4.28	1.50	0.63	S13	0.04	5.70	3.12	2.29
W14	BDL	6.40	1.59	0.97	S14	BDL	2.14	0.72	0.48
W15	BDL	2.65	0.33	0.04	S15	BDL	3.45	2.86	0.64
W16	BDL	6.12	0.83	0.01	S16	BDL	1.17	0.25	0.04

Table S4. Concentrations of target compounds in water (ng/L) samples from the Songhua River, North China.

PAHs	**Abbreviation**	**Ring nu**	**Min**	**Max**	**Median**	**STD**	**Skewness**	**Kurtosis**
Naphthalene	NaP	2	56.7	188	98.7	43.5	0.57	−0.98
Acenaphthylene	Acy	2	2.72	22.3	12.0	6.27	0.29	−1.12
Acenaphthene	Ace	3	3.53	15.3	8.68	3.22	0.43	−0.14
Fluorene	Flu	3	18.3	57.1	29.9	11.2	0.77	0.06
Phenanthrene	Phe	3	33.0	120	54.0	25.3	1.00	0.41
Anthracene	Ant	3	2.67	10.4	5.74	2.41	0.53	−0.37
Fluoranthene	Fluo	4	6.61	34.6	11.2	7.93	1.30	1.20
Pyrene	Pyr	4	4.75	31.2	7.92	7.54	1.54	2.14
Benz[a]anthracene	BaA	4	1.44	12.6	3.26	3.02	1.87	3.52
Chrysene	Chr	4	1.45	10.1	3.31	2.87	1.14	0.14
Benzo[b]fluoranthene	BbF	5	1.97	16.0	4.06	4.53	1.60	1.19
Benzo[k]fluoranthene	BkF	5	1.68	13.8	4.37	3.36	1.77	2.79
Benzo[a]pyrene	BaP	5	BDL	11.0	3.61	2.68	1.16	1.88
Indeno[1,2cd]pyrene	IcdP	6	BDL	8.52	2.45	2.36	1.44	2.09
Dibenzo[a,h]anthrathene	DahA	5	BDL	2.22	0	0.67	1.97	3.11
Benzo[g,h,i]perylene	BghiP	6	BDL	8.47	3.12	2.25	1.13	1.18
∑PAHs	-	-	135	562	252	129	18.6	17.10
∑2-3 ring	-	-	117	413	209	92.1	3.62	−2.14
∑4-6ring	-	-	17.9	148	43.3	37.2	14.9	19.20
LMW/HMW	-	-	6.53	2.78	4.81	2.47	0.24	−0.11
∑PAHcarc	-	-	6.54	74.5	21.3	19.5	10.9	14.70
Me-PAHs								
2-Methylnaphthalene.	2-MNAP	2	BDL	49.6	26.6	12.3	−0.47	0.83
1-Methylnaphalene.	1-MNAP	2	BDL	34.7	18.4	8.28	−0.13	1.19
2,6-Dimethylnaphthalene	2,6-DMNAP	2	0.38	14.3	6.41	3.05	0.56	2.36
2,7-Dimethylnaphthalene	2,7-DMNAP	2	0.38	14.3	6.41	3.05	0.56	2.36
1,3-Dimethylnaphthalene	1,3-DMNAP	2	0.3	16.4	8.95	3.86	−0.02	1.09
1,6-Dimethylnaphthalene	1,6-DMNAP	2	BDL	10.2	3.45	2.50	1.28	2.39
1,4-Dimethylnaphthalene	1,4-DMNAP	2	0.33	6.48	3.19	1.54	0.45	0.88
1,5-Dimethylnaphthalene	1,5-DMNAP	2	0.22	4	1.68	0.89	0.76	1.51
1,2-Dimethylnaphthalene	1,2-DMNAP	2	BDL	5.34	2.70	1.24	0.29	1.77

2-Methylphenanthrene.	2-MPHE	3	0.51	5.62	1.508	1.47	1.21	1.02
2-Methylanthracene	2-MANT	3	1.26	7.69	2.76	1.86	1.07	0.66
1-Methylanthracene	1-MANT	3	0.09	4.3	1.13	1.16	1.24	1.11
1-Methylphenanthrene	1-MPHE	3	BDL	1.15	BDL	0.32	2.70	6.86
9-Methylanthracene	9-MANT	3	BDL	44.6	30.5	10.6	−1.13	2.52
3,6-Dimethylphenanthrene	3,6-DMPHE	3	0.22	1.24	0.50	0.32	0.87	−0.34
2,3-Dimethylanthracene	2,3-DMA	3	BDL	0.41	0.08	0.12	1.09	0.26
9,10-Dimethylanthracene	9,10-DMA	3	0.86	19.9	8.36	6.53	0.36	−1.13
9-Methylphenylfluorene	9-MMHEN	3	BDL	2.76	0.00	0.68	3.99	15.9
2-Methylfluoranthene	2-MFLU	4	0.1	3.43	0.30	0.93	1.97	3.86
1-Methylpyrene	1-MPYR	4	0.03	1.34	0.18	0.47	0.73	−1.23
1,2-Methylbenzaanthracene	1,2-MBaA	4	BDL	1.19	BDL	0.30	3.27	11.5
7,9-Methylbenzaanthracene	7,9-MBaA	4	BDL	3.8	BDL	1.28	1.04	−0.24
4,6-Methylbenzaanthracene	4,6-MBaA	4	BDL	1.77	BDL	0.52	1.89	3.30
3,5-Methylbenzaanthracene	3,5-MBaA	4	BDL	35.5	BDL	16.6	0.89	−1.38
10-Methylbenzaanthracene	10-MBaA	4	BDL	20.7	BDL	8.15	1.77	1.29
5,8-Dimethylbenzocphenanthrene	5,8-DMBcPH	4	BDL	2.8	BDL	0.98	1.56	1.22
6,8-Dimethylbenzaanthracene	6,8-DMBaA	4	BDL	3.02	BDL	0.98	1.97	2.66
3,9-Dimethylbenzaanthracene	3,9-DMBaA	4	BDL	0.72	BDL	0.25	1.85	1.83
7,12-Dimethylbenzaanthracene	7,12-DMBaA	4	BDL	0.65	BDL	0.19	2.11	4.1
3-Methylcholanthrene	3-MCHA	3	BDL	14.3	1.65	5.79	0.73	−1.28
8,9-Methylbenzoapyrene	8,9-MCHA	3	BDL	17.7	0.56	4.81	2.52	6.55
7,10-Methylbenzoapyrene	7,10-MBaP	5	BDL	2.78	BDL	0.74	2.44	6.71
7,10-Dimethylbenzoapyrene	7,10-DMBaP	5	BDL	2.25	0.35	0.81	0.74	−1.03
∑Me-PAHs	-	-	9.36	711	126	206	80.5	158
∑2-3 ring	-	-	4.55	243	122	59.9	14.7	41.3
∑4-6ring	-	-	4.81	467	3.06	145	65.8	117
LMW/HMW	-	-	0.94	0.52	40.1	0.41	0.22	0.35
NPAHs								
1-Nitronaphthalene	1-NN	2	BDL	1.67	1.10	0.50	1.34	1.09
2-Nitronaphthalene	2-NN	2	BDL	5.39	0.10	1.59	1.68	2.39
2-Nitrobiphenyl	2-NBP	2	BDL	5.28	0.06	1.85	0.81	−0.80
4-Nitrobiphenyl	4-NBP	2	BDL	0.54	BDL	0.15	1.14	0.56
5-Nitroacenaphthene	5-NAC	3	BDL	1.11	0.16	0.33	1.62	1.82
2,2'-Dinitrobiphenyl	2,2'-DBP	2	BDL	0.11	BDL	0.02	3.87	15.2
9-Nitroanthracene	9-NAN	3	BDL	13.2	0.16	3.85	2.46	5.44
9-Nitrophenanthrene	9-NPH	3	BDL	4.59	0.69	1.14	2.58	8.14
2-Nitrodibenzothiophene	2-NDB	3	0.03	1.36	0.26	0.40	1.30	0.93
3-Nitrophenanthrene	3-NPH	3	0.12	2.86	0.40	0.66	3.03	10.4
2-Nitroanthracene	2-NAN	3	0.39	11.5	3.96	3.47	0.59	−0.81
9,10-Dinitroanthracene	9,10-DNAN	3	0.72	8.8	3.31	2.82	0.49	−1.21
∑NPAHs	-	-	1.26	56.5	10.2	7.35	5.41	11.3

Table S5. Concentrations of target compounds in sediment (ng/g dw) samples from the Songhua River, North China.

PAHs	Abbreviation	Ring nu	Min	Max	Median	STD	Skewness	Kurtosis
Naphthalene	NaP	2	1.74	55.8	20.0	14.9	0.74	0.49
Acenaphthylene	Acy	2	0.14	19.2	1.39	4.53	3.70	14.3
Acenaphthene	Ace	3	0.3	6.06	2.90	1.59	0.07	−0.56
Fluorene	Flu	3	2.57	19.5	11.5	4.59	−0.2	−0.21
Phenanthrene	Phe	3	14.6	112	36.3	27.3	1.44	1.78
Anthracene	Ant	3	1.19	36.4	3.75	8.49	3.38	12.3
Fluoranthene	Fluo	4	6	382	13.0	92.2	3.68	14.1
Pyrene	Pyr	4	4.84	250	16.2	59.4	3.58	13.5
Benz[a]anthracene	BaA	4	0.63	183	4.11	44.6	3.84	15.0
Chrysene	Chr	4	0.34	158	5.45	38.5	3.60	13.6
Benzo[b]fluoranthene	BbF	5	1.43	213	5.10	52.1	3.70	14.2
Benzo[k]fluoranthene	BkF	5	0.6	66.8	1.28	16.3	3.77	14.6
Benzo[a]pyrene	BaP	5	0.6	163	2.18	40.2	3.85	15.1
Indeno[1,2,3-cd]pyrene	IcdP	6	0.35	172	2.51	42.5	3.79	14.7
Dibenz[a,h]anthracene	DahA	5	0.21	32.8	0.51	8.06	3.82	14.9
Benzo[g,h,i]perylene	BghiP	6	0.22	126	2.31	31.0	3.70	14.2
∑PAHs	-	-	35.8	200	129	486	46.5	172
∑2-3 ring	-	-	20.6	249	76.1	61.4	9.14	28.1
∑4-6ring	-	-	15.2	1750	52.7	425	37.3	144
LMW/HMW	-	-	1.35	0.14	1.44	0.14	0.24	0.19

∑PAHcarc	-	-	4.16	988	20.9	242	26.4	102
Me-PAHs								
Methylnaphthalene.2	2-MNAP	2	BDL	23.2	9.69	5.29	0.30	1.59
Methylnaphalene.1	1-MNAP	2	BDL	15.6	5.59	3.52	0.76	2.26
Dimethylnaphthalene2.6	2,6-DMNAP	2	BDL	8.32	2.60	2.00	1.55	3.16
Dimethylnaphthalene2.7	2,7-DMNAP	2	0.1	8.32	2.60	1.99	1.58	3.21
Dimethylnaphthalene1.3	1,3-DMNAP	2	0.31	13.8	4.07	2.90	2.20	7.54
Dimethylnaphthalene1.6	1,6-DMNAP	2	BDL	13.9	2.88	3.12	2.86	9.99
Dimethylnaphthalene1.4	1,4-DMNAP	2	BDL	6.12	1.76	1.32	2.29	7.78
Dimethylnaphthalene1.5	1,5-DMNAP	2	0.04	5.03	1.03	1.12	3.02	10.9
Dimethylnaphthalene1.2	1,2-DMNAP	2	BDL	4.8	1.10	1.05	2.75	9.54
Methylphenanthrene.2	2-MPHE	3	BDL	14.1	0.95	4.32	2.39	4.58
Methylanthracene.2	2-MANT	3	0.15	21.1	1.94	5.47	2.65	6.94
Methylanthracene.1	1-MANT	3	BDL	13.1	0.91	3.59	2.38	5.36
Methylphenanthrene.1	1-MPHE	3	BDL	11.3	0.82	3.41	2.31	4.43
Methylanthracene.9	9-MANT	3	BDL	62.5	7.33	15.2	2.79	8.44
Dimethylphenanthrene3.6	3,6-DMPHE	3	BDL	5.38	0.32	1.31	3.13	10.7
Dimethylanthracene2.3	2,3-DMA	3	BDL	1.49	0.08	0.39	2.39	5.85
Dimethylanthracene9.10	9,10-DMA	3	BDL	0.77	0.05	0.21	1.77	3.39
Methylphenylfluorene9.9	9-MMHEN	3	BDL	0.1	0.00	0.02	3.48	12.7
Methylfluoranthene.2	2-MFLU	4	0.02	13.6	0.30	4.43	2.38	4.48
Methylpyrene.1	1-MPYR	4	BDL	12.3	0.37	3.52	2.34	5.02
Methylbenzaanthracene1.2	1,2-MBaA	4	BDL	7.08	0.05	1.94	2.80	7.62
Methylbenzaanthracene7.9	7,9-MBaA	4	BDL	31.2	0.74	8.38	2.91	8.42
Methylbenzaanthracene4.6	4,6-MBaA	4	BDL	8.71	0.25	2.41	2.71	6.93
Methylbenzaanthracene3.5	3,5-MBaA	4	BDL	11.2	6.17	3.68	−0.33	−1.05
Methylbenzaanthracene10	10-MBaA	4	BDL	10.3	3.42	3.14	0.93	0.58
Dimethylbenzocphenan-threne5.8	5,8-DMBcPH	4	BDL	14.8	0.60	3.67	3.32	11.7
Dimethylbenzaanthra-cene6.8	6,8-DMBaA	4	BDL	5.75	0.21	1.55	2.70	7.18
Dimethylbenzaanthra-cene3.9	3,9-DMBaA	4	BDL	9	0.27	2.31	3.04	9.66
Dimethylbenzaanthra-cene7.12	7,12-DMBaA	4	BDL	4.8	0.17	1.20	3.35	11.8
Methylcholanthrene3	3-MCHA	3	BDL	4.6	0	1.15	4	16
Methylbenzoapyrene8.9	3,9-MCHA	3	BDL	25.3	0.54	7.30	2.52	5.68
Methylbenzoapyrene7.10	7,10-MBaP	5	BDL	4.65	0.29	1.52	2.42	4.61
Dimethylbenzoapyrene7.10	7,10-DMBaP	5	BDL	1.58	0	0.39	3.74	14.4
∑Me-PAHs			0.62	394	57.2	103	79.5	231
∑2-3 ring			0.6	259	43.7	64.8	47.2	140
∑4-6ring			0.02	135	13.4	38.2	32.3	91.5
LMW/HMW			30	1.91	3.25	1.69	1.45	1.53
NPAHs								
1-Nitronaphthalene	1-NN	2	BDL	0.58	1.28	0.14	2.79	9.10
2-Nitronaphthalene	2-NN	2	BDL	0.65	0.01	0.20	1.67	1.91
2-Nitrobiphenyl	2-NBP	2	BDL	9.74	0.05	2.26	3.07	10.7
4-Nitrobiphenyl	4-NBP	2	BDL	0.13	0.00	0.03	1.87	3.97
5-Nitroacenaphthene	5-NAC	3	BDL	1.91	0.11	0.45	3.50	13.1
2,2'-Dinitrobiphenyl	2,2'-DBP	2	BDL	0.05	0	0.01	1.49	0.47
9-Nitroanthracene	9-NAN	3	BDL	23.9	0.30	5.87	3.65	13.9
9-Nitrophenanthrene	9-NPH	3	BDL	19.6	0.90	4.81	3.42	12.4
2-Nitrodibenzothiophene	2-NDB	3	BDL	0.22	0.00	0.05	3.53	13.1
3-Nitrophenanthrene	3-NPH	3	BDL	1.24	0.10	0.32	2.22	5.69
2-Nitroanthracene	2-NAN	3	0.28	56.7	0.91	13.9	3.97	15.8
9,10-Dinitroanthracene	9,10-DNAN	3	BDL	55.4	1.74	17.9	2.48	4.84
∑NPAHs			0.28	170	5.4	45.9	33.6	104

Table S6. Physicochemical characteristics of sediment and water samples.

Sediment	Tem. (°C)	Pres (mmHg)	Dissolved oxygen (%)	Conductivity (mS/cm)	TDS (g/L)	Salinity (PSU)	pH	DOC (mg/L)	TOC (%)
S1	13.6	754	93.7	172	0.11	0.08	6.7	4.60	5.16
S2	25.8	755	79.8	174	0.11	0.08	7.09	5.86	19.6
S3	29.3	756	100	162	0.11	0.07	7.99	4.85	5.02
S4	25.8	755	87.2	212	0.14	0.1	7.45	4.45	6.16
S5	27.4	759	85.8	265	0.17	0.12	7.15	9.35	11.4
S6	24	754	102	122	0.08	0.06	7.37	4.41	4.59
S7	27.3	761	112	217	0.14	0.1	8.62	5.94	5.87
S8	23.2	762	92	177	0.12	0.08	7.57	5.74	6.79
S9	13.3	767	102	151	0.1	0.07	7.66	5.3	5.8
S10	22.1	758	100	93.9	0.06	0.04	7.1	9.67	9.83
S11	17.9	759	127	109	0.07	0.05	8.16	7.51	4.94
S12	24.1	753	88	131	0.09	0.06	7.04	7.17	10.4
S13	21	757	92.7	255	0.17	0.12	7.05	4.21	5.28
S14	23.1	762	103	69.1	0.04	0.03	7.87	8.05	8.54
S15	20.9	765	95.7	202	0.13	0.09	7.74	5.45	5.11
S16	27.7	759	107	155	0.1	0.07	7.37	6.04	6.05
Min	13.3	753	79.8	69.1	0.04	0.03	6.7	4.21	4.59
Max	29.3	767	127	265	0.17	0.12	8.62	9.67	19.6
Mean	22.7	759	98.8	167	0.10	0.07	7.51	6.25	8.04
Water									
W1	12.6	750	8.8	69.1	0.04	0.03	6.62	3.63	4.34
W2	29.3	855	127	653	0.42	0.32	8.62	14.3	19.6
W3	23.0	761	95.3	186	0.12	0.08	7.49	5.73	7.21
W4	3.73	15.1	17.7	90.1	0.05	0.04	7.02	1.89	3.43
W5	23.1	759	97.4	172	0.11	0.08	7.65	5.3	5.87
W6	21	755	88	144	0.09	0.07	7.13	4.78	5.06
W7	25.8	765	103	203	0.13	0.09	7.75	5.89	7.89
W8	12.6	750	8.8	69.1	0.04	0.03	6.62	3.63	4.34
W9	29.3	855	127	653	0.42	0.32	8.62	14.3	19.6
W10	23.0	761	95.8	186	0.12	0.08	7.49	5.73	7.21
W11	3.74	15.1	17.8	90.1	0.05	0.04	7.31	1.89	3.44
W12	23.1	759	97.4	172	0.11	0.08	7.65	5.3	5.87
W13	21	755	88	144	0.09	0.07	7.13	4.78	5.06
W14	25.8	765	103	203	0.13	0.09	7.75	5.89	7.89
W15	21	755	102	189	0.42	0.2	7.37	4.41	7.51
W16	20.6	757	89.5	171	0.13	0.12	7.05	8.37	11.4
Min	3.73	15.1	8.8	69.1	0.04	0.03	6.62	1.89	3.43
Max	29.3	855	127	653	0.42	0.32	8.62	14.3	19.6
Mean	19.54	650	78.1	228	0.16	0.11	6.38	6.23	8.26

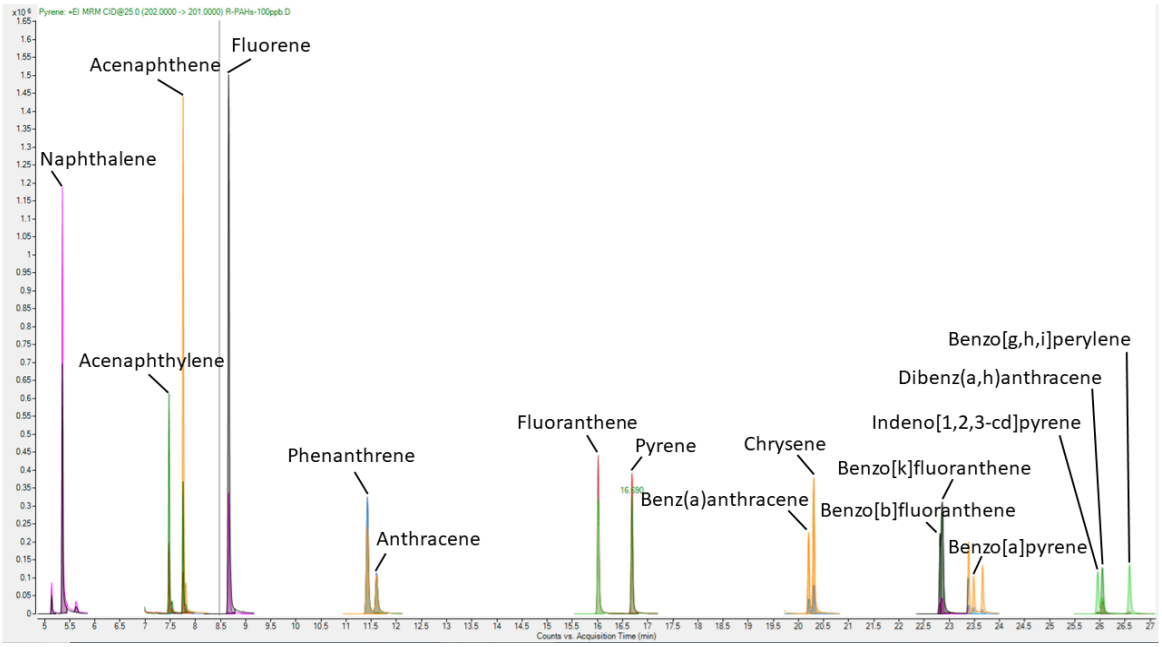
Table S7. Factor pattern of PCA for PAHs in water, sediment, of the Songhua River Basin, China.

PAHs	Water			Sediment	
	PC1	PC2	PC3	PC1	PC2
NaP	0.48	0.61	0.25	0.15	0.94
Acy	0.57	0.65	−0.40	0.99	0.02
Ace	0.3	0.70	0.35	0.37	0.88
Flu	0.58	0.78	0.00	0.30	0.82
Phe	0.72	0.30	0.40	0.75	0.121
Ant	0.50	0.49	0.20	0.99	0.02
Fluo	0.95	−0.09	−0.23	0.99	−0.11
Pyr	0.92	−0.14	−0.28	0.99	−0.07
BaA	0.87	−0.01	−0.3	0.99	−0.11
Chr	0.91	−0.29	0.10	0.99	−0.06
BbF	0.79	−0.24	0.25	0.99	−0.06
BkF	0.64	0.49	−0.24	0.99	−0.09
BaP	0.85	−0.33	−0.09	0.99	−0.09

IcdP	0.65	−0.69	0.26	0.99	−0.09
DahA	0.76	−0.48	0.08	0.99	−0.08
BghiP	0.79	−0.40	0.07	0.99	−0.07
%Variance	53.5	22.8	6.33	79.0	15.2

Table S8. PAHs TEQ concentrations in different sediment sites (ng/g dw).

Summer																	
PA-H$_{scarc}$	**TEF**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**	**S16**
BaA	0.1	0.14	1.29	0.31	0.15	2.59	0.41	1.79	0.63	0.41	0.71	0.84	0.06	0.36	0.30	0.11	18.3
Chr	0.01	0.02	0.17	0.06	0.02	0.33	0.03	0.25	0.02	0.11	0.05	0.16	BDL	0.02	0.05	BDL	1.58
BbF	0.1	0.31	1.24	1.27	0.15	3.99	0.23	3.16	0.33	1.00	0.38	1.71	0.45	0.25	0.56	0.14	21.3
BkF	0.1	0.17	0.25	0.14	0.07	0.93	0.09	1.10	0.11	0.18	0.09	0.35	0.10	0.06	0.11	0.06	6.68
BaP	1	0.60	5.87	3.77	0.77	21.4	1.03	16.4	1.43	3.76	1.44	7.43	1.06	0.71	2.93	1.07	163
DahA	1	0.43	1.03	0.74	0.38	4.37	0.21	4.44	0.47	1.02	0.27	0.97	0.23	0.32	0.55	0.26	32.8
BghiP	0.01	0.01	0.04	0.04	BDL	0.18	BDL	0.23	0.01	0.04	0.01	0.06	BDL	BDL	0.02	BDL	1.26
Min		0.01	0.04	0.04	BDL	0.18	BDL	0.23	0.01	0.04	0.01	0.06	BDL	BDL	0.02	BDL	1.26
Max		0.60	5.87	3.77	0.77	21.4	1.03	16.4	1.43	3.76	1.44	7.43	1.06	0.71	2.93	1.07	163
Mean		0.24	1.41	0.90	0.22	4.83	0.29	3.91	0.43	0.93	0.42	1.64	0.27	0.24	0.64	0.23	35.1
∑ TE-Q$_{carc}$		1.70	9.91	6.34	1.55	33.8	2.03	27.4	3.01	6.53	2.97	11.5	1.92	1.74	4.54	1.66	246
Winter																	
BaA	0.1	0.02	0.07	0.04	0.12	0.14	0.19	0.32	0.19	0.59	0.37	0.81	0.22	0.42	0.28	0.20	0.54
Chr	0.01	BDL	BDL	BDL	BDL	0.33	0.03	0.04	0.01	0.08	0.03	0.05	0.02	0.03	0.06	0.01	0.01
BbF	0.1	0.03	0.04	0.04	0.13	0.35	0.23	0.52	0.38	1.10	0.29	1.60	0.25	0.39	0.40	0.47	0.20
BkF	0.1	0.03	0.12	0.04	0.06	0.22	0.29	0.33	0.11	0.47	0.26	0.98	0.47	0.20	0.59	0.28	0.16
BaP	1	3.61	5.85	3.44	11.0	1.67	3.69	0.70	1.43	8.30	2.91	5.53	1.01	3.02	5.75	3.06	2.10
DahA	1	0.1	0.60	0.20	2.21	0.10	0.55	0.40	0.47	1.39	0.24	0.30	0.10	0.09	1.26	0.90	1.34
BghiP	0.01	BDL	BDL	BDL	BDL	0.01	0.03	0.03	0.01	0.05	0.02	0.02	BDL	0.01	0.04	0.02	0.01
Min		BDL	BDL	BDL	BDL	0.01	0.03	0.03	0.01	0.05	0.02	0.02	BDL	0.01	0.04	0.01	0.01
Max		3.61	5.85	3.44	11.0	1.67	3.69	0.7	3.61	8.30	2.91	5.53	1.06	3.02	5.75	3.06	2.10
Mean		0.54	0.95	0.53	1.93	0.33	0.73	0.33	0.65	1.71	0.60	1.33	0.27	0.59	1.20	0.70	0.62
∑TE-Q$_{carc}$		3.79	6.69	3.77	13.5	2.37	5.15	2.35	4.59	11.9	4.21	9.31	1.92	4.19	8.41	4.95	4.40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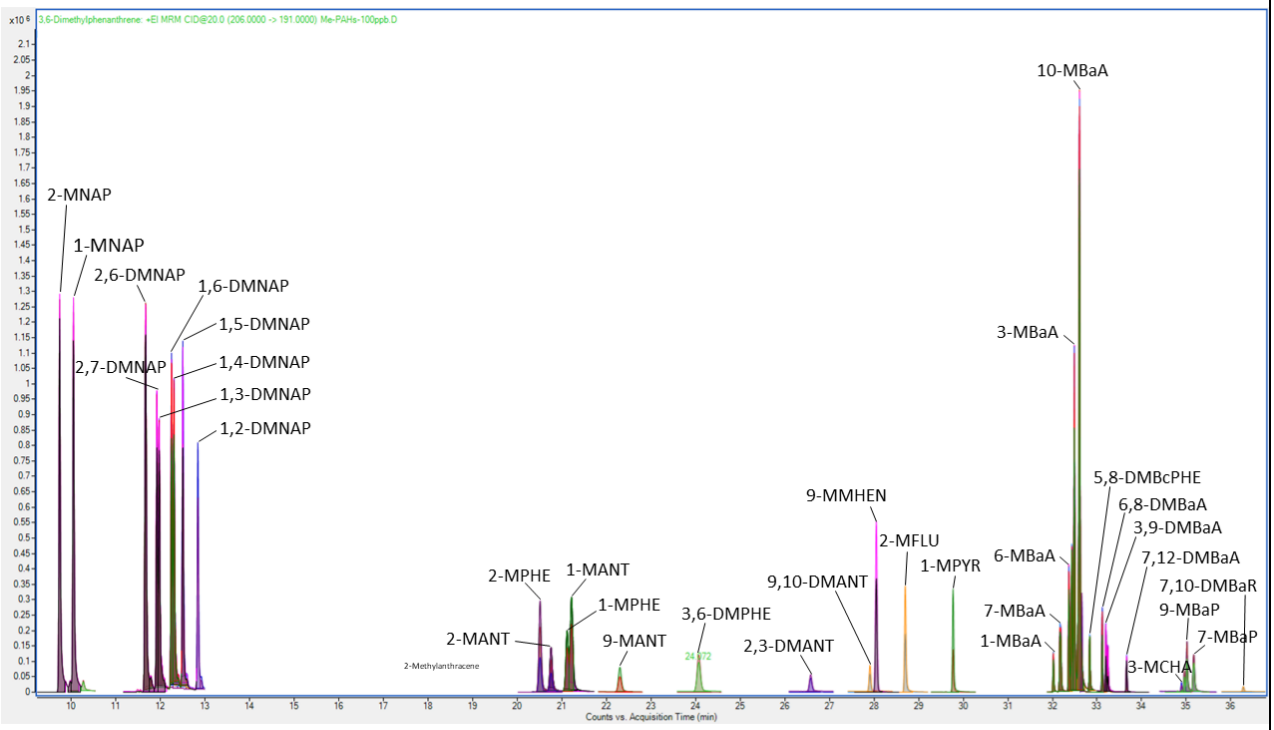
Naphthalene
Acenaphthene
Fluorene
Acenaphthylene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Dibenz(a,h)anthracene
Benzo[g,h,i]perylene
Counts vs. Acquisition Time (min)

(**a**)


3,6-Dimethylphenanthrene: +EI MRM CID@20.0 (206.0000 -> 191.0000) Me-PAHs-100ppb.D
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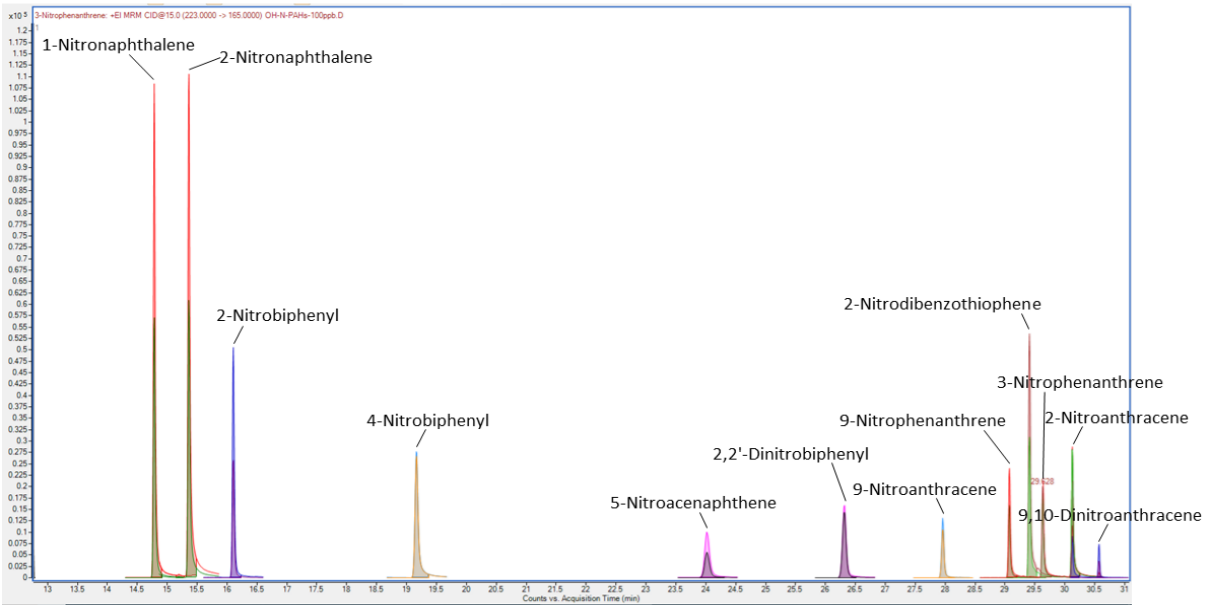
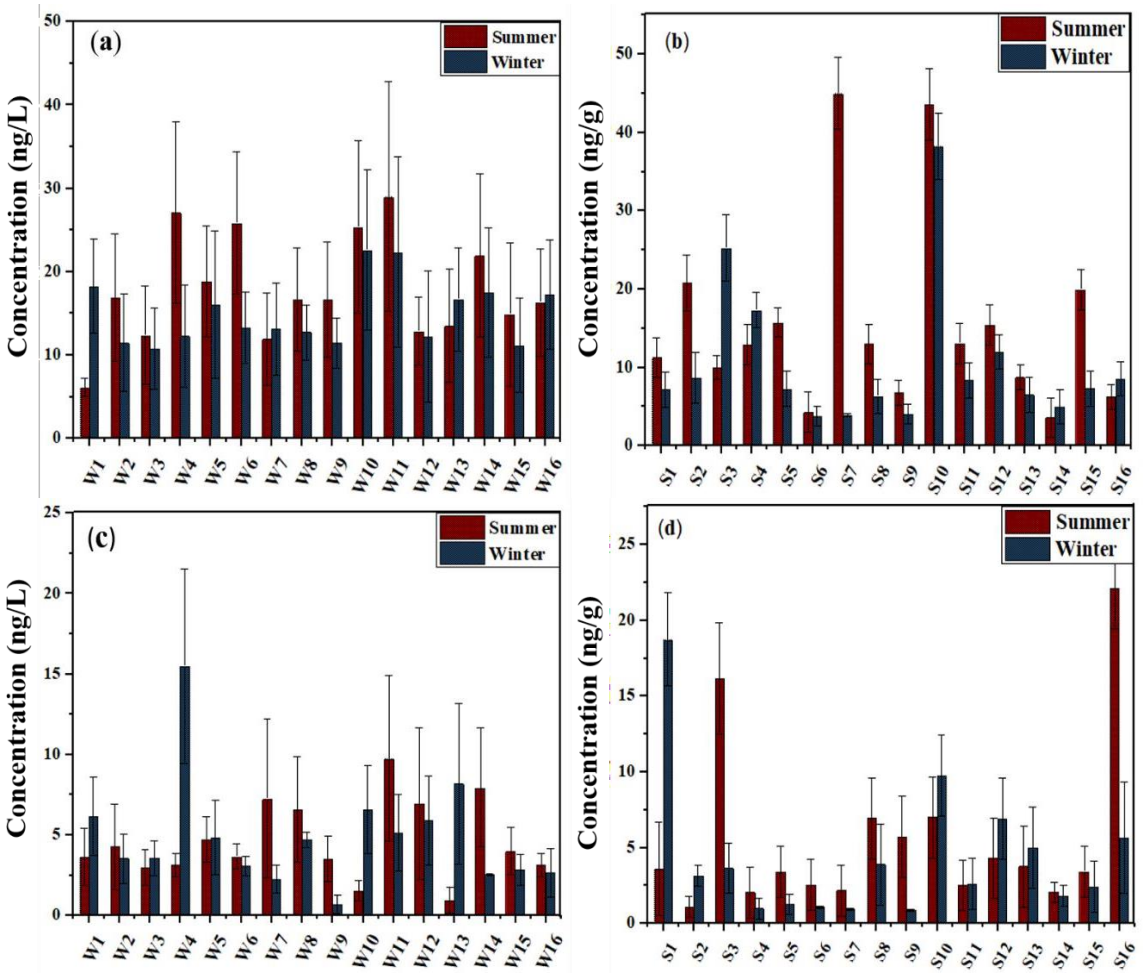
1-MNAP
2,6-DMNAP
1,6-DMNAP
1,5-DMNAP
2,7-DMNAP
1,4-DMNAP
1,3-DMNAP
1,2-DMNAP
2-MPHE
1-MANT
1-MPHE
2-MANT
9-MANT
2-Methylanthracene
3,6-DMPHE
9,10-DMANT
2,3-DMANT
9-MMHEN
2-MFLU
1-MPYR
10-MBaA
3-MBaA
6-MBaA
7-MBaA
1-MBaA
5,8-DMBcPHE
6,8-DMBaA
3,9-DMBaA
7,12-DMBaA
7,10-DMBaR
9-MBaP
7-MBaP
3-MCHA
Counts vs. Acquisition Time (min)

(**b**)



(**c**)

Figure S1. The representative chromatograph of (**a**) PAHs, (**b**) Me-PAHs and (**c**) NPAH.



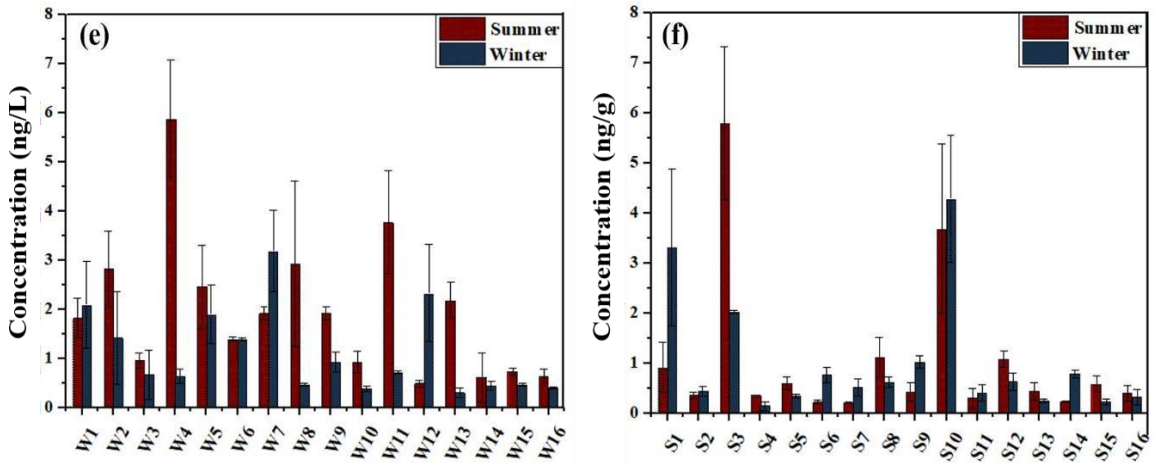


Figure S2. Average concentrations of Σ16 PAHs (**a**) water (ng/L), (**b**) sediment (ng/g), ∑33 Me-PAHs (**c**) water (ng/L), (**d**) sediment (ng/g), and ∑12 NPAHs (**e**) water (ng/L), (**f**) sediment (ng/g), at 16 sampling sites during the summer and winter seasons.

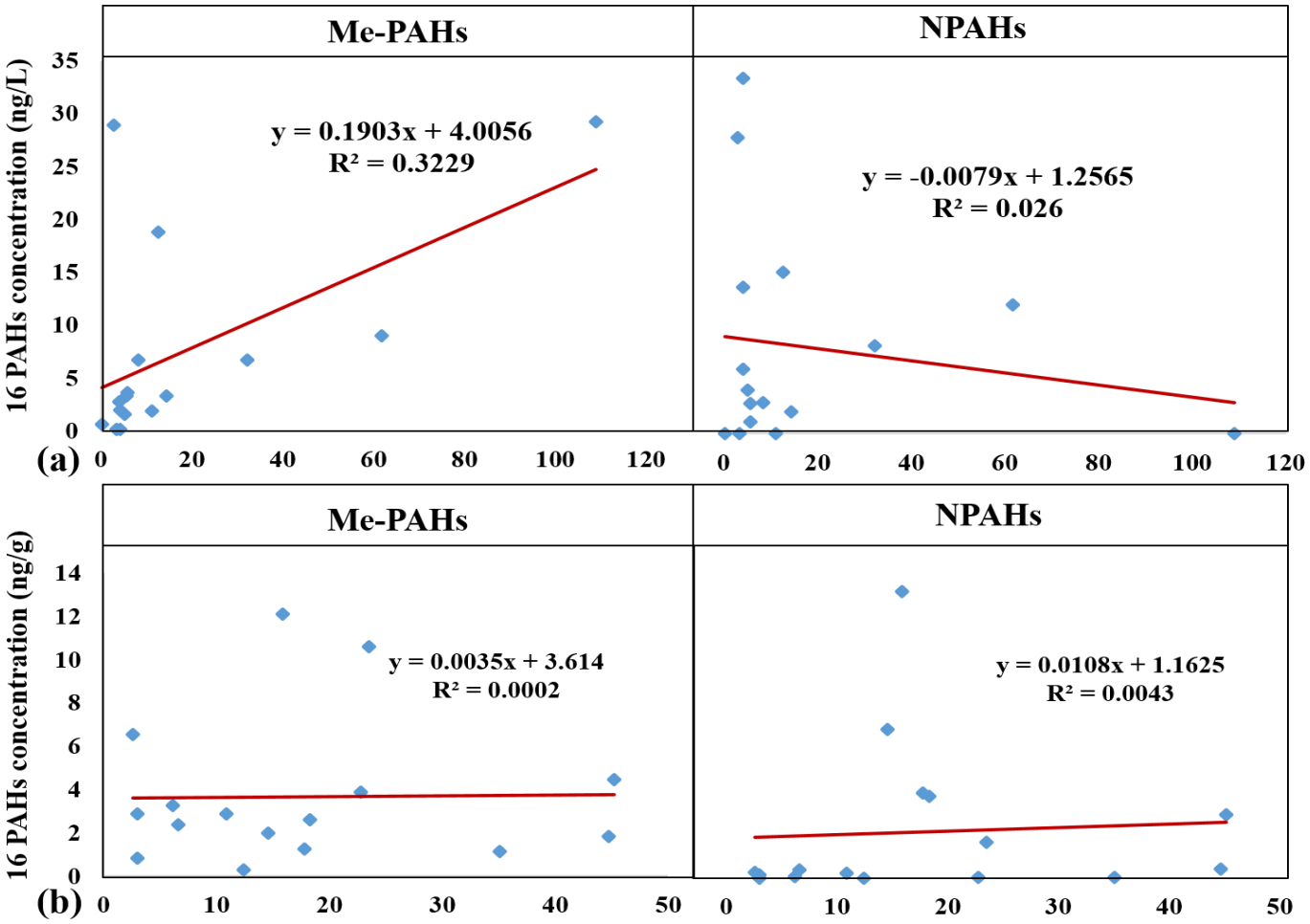


Figure S3. Scatterplot of Σ16 PAHs VS ∑33 Me-PAHs and ∑14 NPAHs, (**a**) water and (**b**) sedimen.