Supporting Information

Formation and Evolution of Solvent-Extracted and Nonextractable Environmentally Persistent Free Radicals in Fly Ash of Municipal Solid Waste Incinerators

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Text: 1

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Text S1. Sodium chloride (NaCl), sodium acetate (NaAc), sodium hydroxide (NaOH), sodium diphosphate ($Na_4P_2O_7$), hydrochloride acid (HCl, 36~38 %), nitric acid (HNO_3, 68%), and hydrofluoric acid (HF, 40%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Phenanthrene (98%) and other PAC, 5,5-Dimethyl-1-pyrrolidine N-oxide (DMPO, 97%), NaN_3 (99%), tert-butanol (TBA, 99%), and *p*-benzoquinone (*p*-BQ, 99%) were purchased from Sigma-Aldrich (Shanghai, China). Acetone, dichloromethane, ethanol, hexane and methanol are HPLC-grade, and these solvents were acquired from China National Medicines Corporation Ltd (Beijing, China). All the chemicals were used as received without further purification.

Table S1. Contents (g kg^{-1}) of C, N, and H in original fly ash samples collected from different municipal solid waste incinerator facilities in China.

	A	B	C	D	E	F	G	H	I	J	K
C	48.35	38.04	96.92	27.03	89.14	65.83	70.96	94.91	23.02	26.86	27.58
H	5.35	4.28	7.46	4.09	6.37	5.92	6.61	8.05	3.54	4.77	2.20
N	0.84	0.64	1.49	0.44	1.75	0.84	1.27	0.07	0.07	0.09	0.13

Table S2. Elemental concentrations (g kg^{-1}) in original fly ash samples obtained from different municipal solid waste incinerator facilities in China.

	A	B	C	D	E	F	G	H	I	J	K
Si	135.31	146.86	125.92	151.85	153.63	177.35	112.34	125.68	184.32	132.44	124.27
Al	69.24	73.51	59.97	84.13	92.42	85.72	72.90	62.35	93.43	96.21	87.02
Ca	145.24	151.86	149.35	140.56	152.03	157.94	143.02	135.40	146.09	155.91	153.47
K	11.54	12.34	12.03	11.17	12.46	12.59	11.33	10.86	10.92	11.79	11.38

Table S3. Metal contents (mg kg^{-1}) in original fly ash samples obtained from different municipal solid waste incinerator facilities in China.

Samples	Cu	Zn	Fe	Cd	Mn	Ti	V	Cr	Ag
A	872 ±20.3	5777 ±42.2	5634 ±94.3	73.2 ±6.7	116 ±14.9	456 ±48.8	8.5 ±7.7	51.9 ±11.1	2.2 ±2.2
B	1238 ±23.9	9311 ±55.9	7532 ±106	110 ±8.2	248 ±23.8	760 ±63.3	34.1 ±11.8	109 ±14.9	17.6 ±3.0
C	975 ±21.8	11096 ±5.5	3699 ±77.5	109 ±8.2	104 ±14.4	458 ±47.8	22.4 ±10.9	61.2 ±11.5	7.1 ±2.8
D	1882 ±26.0	16178 ±38.0	34195 ±210	37.8 ±5.0	1241 ±47.2	3541 ±113	41.9 ±16.5	212 ±18.3	17.0 ±2.5
E	708 ±16.4	7398 ±44.4	4117 ±71.9	128 ±8.9	173 ±17.7	892 ±69.4	26.4 ±9.6	66 ±12.6	5.5 ±2.8
F	625 ±16.6	7444 ±46.3	4046 ±77.6	89.7 ±7.4	170 ±18.4	621 ±57.6	25.8 ±10.2	38.7 ±10.1	2.3 ±2.3
G	710 ±18.3	9755 ±58.5	3801 ±77.3	122 ±8.5	118 ±15.2	419 ±47.2	30.3 ±10.4	33.5 ±9.4	13.7 ±2.7
H	860 ±19.2	9261 ±55.6	4487 ±79.4	99.3 ±8.2	142 ±16.8	664 ±62.0	24.4 ±10.3	60.4 ±12.5	7.6 ±3.0
I	854 ±18.8	4241 ±33.7	12767 ±131	62.6 ±6.6	830 ±42.7	2103 ±103	57.5 ±14.0	174 ±19.2	5.7 ±2.8
J	1367 ±22.6	10495 ±63.0	17878 ±144	159 ±10.2	488 ±31.3	2209 ±103	42.1 ±15.9	295 ±24.1	9.6 ±3.4
K	1375 ±53.5	13657 ±342	22185 ±363	114 ±12.5	574 ±35.6	2974 ±284	136 ±43.6	135 ±14.2	12.3 ±1.4

Table S4. List of the identified organic compounds in original fly ash samples obtained from municipal solid waste incinerator facilities in China.

Type of contaminants	Detected compounds
Alkylated benzene	Methylbenzene, Ethylbenzene, Xylene, and 1-ethyl-2-methyl-Benzene
PAHs	Naphthalene, Fluorine, Phenanthrene, Anthracene, Fluoranthene, Chrysene, Pyrene, Pyrylene, Benzo[a]anthracene, Benzo[a]Pyrene, Benzo[e]Pyrene, Benzo[k]fluoranthene, Benzo[ghi]fluoranthene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene, Benzo[a]triphenylene, Benzo[b]triphenylene, Dibenzo[def, mno]chrysene,
Alkylated PAHs	1-Methylnaphthalene, 2-Methylnaphthalene, 1,3-Dimethylnaphthalene, 2,6-dimethylnaphthalene, 2,3,6-trimethylnaphthalene, methylfluorene, 1-Methylphenanthrene, 9-Methylphenanthrene, 2-Methylanthracene, 1-Methylanthracene, 4,5-Dimethylphenanthrene, 1-Methylpyrene, 1,4-Dimethylanthracene, and 2-Methylbenz[a]anthracene
Ketonized/hydroxylated PAHs	Fluorenone, Anthrone, Anthraquinone, Benzo[a]pyrene-quinone, 1-Pyrenol, 9H-Fluoren-9-ol Benzo[a]anthracene-7,12-dione, 1-Methyl-9,10-anthracenedione, 2-Benzanthrone, 7H-Benzo[de]anthracene-7-one,
Phenol and its derivatives	Phenol, 2-Methyl-phenol, 3-Methyl-phenol
Other PAC	3-Pyrenylacetic acid, 4,5-dihydro- Benzo[a]Pyrene, biphenyl, and phenyltoluene.

Table S5. Organic carbon levels in original, nonextractable, and solvent-extracted fly ash samples obtained from different municipal solid waste incinerator facilities in China.

Samples	TOC of original samples	TOC of nonextractable samples	Solvent-extracted organic carbon [a]
A	61.68	48.08	13.60
B	51.07	36.34	14.73
C	110.03	95.52	14.51
D	36.22	24.89	11.33
E	104.23	89.13	15.10
F	76.53	63.29	13.24
G	85.91	70.30	15.61
H	107.19	93.27	13.92
I	31.27	20.51	10.76
J	37.72	24.20	13.52
K	37.82	24.52	13.30

[a] Calculated by the difference between TOC of original samples and TOC of nonextractable samples.

Table S6. Concentrations (spins g^{-1}) and g-factor of free organic radical species on fly ash samples.

Samples	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}
	Original samples		Solvent-extracted EPFRs		Nonextractable EPFRs		Total EPFR (Solvent-extracted + Nonextractable)
A	5.610 ± 0.025	2.0033 ± 0.0002	3.731 ± 0.225	2.0042 ± 0.0001	1.942 ± 0.022	2.0026 ± 0.0003	5.673
B	5.994 ± 0.100	2.0038 ± 0.0001	4.328 ± 0.338	2.0039 ± 0.0004	1.404 ± 0.126	2.0031 ± 0.0001	5.732
C	9.348 ± 0.219	2.0040 ± 0.0001	3.844 ± 0.407	2.0044 ± 0.0003	5.318 ± 0.342	2.0032 ± 0.0002	9.162
D	6.231 ± 0.054	2.0035 ± 0.0002	4.606 ± 0.835	2.0042 ± 0.0002	1.596 ± 0.104	2.0027 ± 0.0002	6.202
E	10.247 ± 0.033	2.0039 ± 0.0003	3.693 ± 0.204	2.0040 ± 0.0002	6.113 ± 0.152	2.0027 ± 0.0003	9.806
F	7.670 ± 0.058	2.0035 ± 0.0001	3.926 ± 0.199	2.0037 ± 0.0002	3.766 ± 0.335	2.0028 ± 0.0001	7.692
G	8.736 ± 0.458	2.0034 ± 0.0001	4.093 ± 0.304	2.0036 ± 0.0003	4.562 ± 0.527	2.0030 ± 0.0002	8.655
H	10.008 ± 0.654	2.0040 ± 0.0001	3.994 ± 0.198	2.0040 ± 0.0002	5.858 ± 0.210	2.0029 ± 0.0004	9.952
I	3.890 ± 0.254	2.0034 ± 0.0001	2.905 ± 0.357	2.0036 ± 0.0004	0.941 ± 0.245	2.0027 ± 0.0003	3.846
J	5.128 ± 0.054	2.0040 ± 0.0001	4.040 ± 0.432	2.0042 ± 0.0003	0.943 ± 0.185	2.0025 ± 0.0004	4.983
K	5.810 ± 0.036	2.0037 ± 0.0003	4.596 ± 0.228	2.0039 ± 0.0002	1.038 ± 0.105	2.0026 ± 0.0002	5.634

Table S7. Concentrations of EPFRs on original fly ash samples during aging under dark conditions.

Samples	0 d		15 d		30 d		45 d	
	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}	g-Factor	S ($\times 10^{15}$) g^{-1}	g-Factor
A	5.610 ±0.025	2.0033 ±0.0002	4.940 ±0.125	2.0034 ±0.0001	4.111 ±0.024	2.0032 ±0.0002	3.521 ±0.014	2.0028 ±0.0002
B	5.994 ±0.100	2.0038 ±0.0001	5.024 ±0.111	2.0035 ±0.0001	4.189 ±0.119	2.0034 ±0.0002	3.39 ±0.024	2.0030 ±0.0001
C	9.348 ±0.219	2.0040 ±0.0001	8.157 ±0.102	2.0036 ±0.0001	6.352 ±0.105	2.0033 ±0.0001	6.330 ±0.335	2.0030 ±0.0002
D	6.231 ±0.054	2.0035 ±0.0002	4.656 ±0.054	2.0035 ±0.0001	3.435 ±0.021	2.0027 ±0.0001	2.661 ±0.662	2.0028 ±0.0001
E	10.247 ±0.033	2.0039 ±0.0003	9.368 ±0.214	2.0034 ±0.0002	8.448 ±0.036	2.0028 ±0.0002	7.632 ±0.210	2.0029 ±0.0001
F	7.670 ±0.058	2.0035 ±0.0001	6.511 ±0.331	2.0033 ±0.0001	5.915 ±0.035	2.0032 ±0.0003	5.260 ±0.054	2.0027 ±0.0002
G	8.736 ±0.458	2.0034 ±0.0001	7.835 ±0.437	2.0037 ±0.0002	7.038 ±0.118	2.0033 ±0.0001	6.330 ±0.036	2.0031 ±0.0001
H	10.008 ±0.654	2.0040 ±0.0001	8.962 ±0.024	2.0034 ±0.0003	8.136 ±0.107	2.0031 ±0.0001	7.62 ±0.054	2.0026 ±0.0002
I	3.890 ±0.254	2.0034 ±0.0001	3.141 ±0.035	2.0035 ±0.0003	2.492 ±0.065	2.0030 ±0.0002	1.861 ±0.055	2.0031 ±0.0001
J	5.128 ±0.054	2.0040 ±0.0001	4.291 ±0.055	2.0035 ±0.0001	3.530 ±0.047	2.0028 ±0.0002	2.669 ±0.147	2.0028 ±0.0002
K	5.810 ±0.036	2.0037 ±0.0003	4.931 ±0.122	2.0032 ±0.0001	4.111 ±0.044	2.0030 ±0.0001	3.248 ±0.217	2.0029 ±0.0003

Table S8. Concentrations of EPFRs on nonextractable samples of fly ash during aging under dark conditions.

Samples	S ($\times 10^{15}$) g^{-1}			
	0 d	15 d	30 d	45 d
A	1.942 ± 0.022	2.014 ± 0.054	1.989 ± 0.034	1.957 ± 0.047
B	1.404 ± 0.126	1.389 ± 0.002	1.387 ± 0.014	1.390 ± 0.055
C	5.318 ± 0.342	5.321 ± 0.047	5.318 ± 0.225	5.300 ± 0.049
D	1.596 ± 0.104	1.568 ± 0.895	1.557 ± 0.124	1.559 ± 0.054
E	6.113 ± 0.152	6.108 ± 0.035	6.007 ± 0.325	6.100 ± 0.047
F	3.766 ± 0.335	3.765 ± 0.054	3.752 ± 0.024	3.749 ± 0.014
G	4.562 ± 0.527	4.558 ± 0.214	4.548 ± 0.558	4.547 ± 0.014
H	5.858 ± 0.210	5.855 ± 0.358	5.852 ± 0.254	5.853 ± 0.108
I	0.941 ± 0.245	1.054 ± 0.054	0.987 ± 0.014	0.925 ± 0.117
J	0.943 ± 0.185	1.008 ± 0.025	0.948 ± 0.365	0.859 ± 0.014
K	1.038 ± 0.105	1.024 ± 0.555	0.998 ± 0.054	1.001 ± 0.248

Table S9. Quantification of various ROS associated with solvent-extracted or nonextractable samples.

Sampling Site	Samples	Amount of various DMPO-ROS on fly ash (spins 10^{15} g^{-1})					
		Singlet oxygen Radical	Hydroxyl Radical	Superoxide Radical	Oxygen-entered Radical	Carbon-centered Radical	Total
A	Solvent-extracted	1.41 ±0.124	4.18 ±0.254	6.13 ±0.215	1.59 ±0.025	5.38 ±0.250	18.67 ±0.354
	Nonextractable	1.13 ±0.215	0.98 ±0.215	4.96 ±0.215	0.19 ±0.245	0.71 ±0.414	7.89 ±0.682
B	Solvent-extracted	1.51 ±0.021	5.46 ±0.325	7.03 ±0.354	1.92 ±0.125	—	15.84 ±0.454
	Nonextractable	2.60 ±0.548	0.78 ±0.121	7.52 ±0.125	—	—	10.92 ±0.575
C	Solvent-extracted	1.82 ±0.015	3.48 ±0.185	6.73 ±0.021	0.39 ±0.090	6.59 ±0.0245	18.82 ±0.105
	Nonextractable	3.30 ±0.312	0.74 ±0.187	7.55 ±0.368	2.60 ±0.324	—	13.86 ±0.424
D	Solvent-extracted	1.41 ±0.154	7.67 ±0.099	7.50 ±0.115	—	2.26 ±0.069	16.52 ±0.195
	Nonextractable	1.95 ±0.122	2.11 ±0.168	1.18 ±0.435	—	4.20 ±0.354	9.37 ±0.451
E	Solvent-extracted	0.80 ±0.100	3.82 ±0.021	5.36 ±0.201	0.92 ±0.121	3.68 ±0.088	14.50 ±0.161
	Nonextractable	3.89 ±0.065	1.28 ±0.098	1.55 ±0.025	1.20 ±0.021	1.16 ±0.245	8.96 ±0.254
F	Solvent-extracted	1.7 ±0.010	5.21 ±0.154	5.90 ±0.089	3.40 ±0.254	3.12 ±0.002	19.25 ±0.258
	Nonextractable	5.30 ±0.208	1.17 ±0.066	5.55 ±0.098	1.21 ±0.035	1.91 ±0.002	15.04 ±0.247
G	Solvent-extracted	3.56 ±0.056	4.51 ±0.201	6.46 ±0.097	2.56 ±0.055	0.24 ±0.012	17.26 ±0.241
	Nonextractable	9.35 ±0.032	1.76 ±0.066	7.33 ±0.124	3.28 ±0.109	0.70 ±0.198	21.09 ±0.206
H	Solvent-extracted	2.10 ±0.078	5.33 ±0.188	5.60 ±0.125	0.30 ±0.064	—	12.96 ±0.198
	Nonextractable	3.18 ±0.012	0.89 ±0.355	1.09 ±0.306	1.28 ±0.234	—	6.38 ±0.367
I	Solvent-extracted	2.51 ±0.025	1.60 ±0.065	3.42 ±0.096	1.89 ±0.214	3.28 ±0.124	12.64 ±0.277
	Nonextractable	4.30 ±0.198	1.62 ±0.012	8.39 ±0.331	1.18 ±0.121	—	15.32 ±0.225
J	Solvent-extracted	2.68 ±0.011	4.90 ±0.054	7.71 ±0.035	2.08 ±0.125	—	17.28 ±0.134
	Nonextractable	3.31 ±0.124	0.77 ±0.011	5.00 ±0.392	1.53 ±0.390	—	10.56 ±0.404
K	Solvent-extracted	1.30 ±0.101	5.78 ±0.198	8.08 ±0.099	0.69 ±0.302	3.48 ±0.035	19.30 ±0.321
	Nonextractable	2.06 ±0.138	1.51 ±0.098	6.29 ±0.401	2.18 ±0.124	1.50 ±0.205	13.44 ±0.544

Table S10. Different free radicals capture efficiency of fly ash.

Sample	Capture efficiency of free radicals (%)				
	Singlet oxygen radical	Hydroxyl radical	Superoxide radical	Oxygen-centered radical	Carbon-centered radical
A	9.70	19.29	41.57	6.55	22.89
B	20.68	16.91	57.06	5.35	—
C	15.56	12.72	42.93	8.88	19.91
D	12.02	34.42	30.66	—	22.90
E	19.67	21.66	29.48	8.93	20.26
F	20.25	18.38	33.56	13.31	14.50
G	32.58	15.91	34.86	14.59	2.06
H	26.98	30.89	34.76	7.37	—
I	23.92	11.58	42.19	10.79	11.52
J	21.29	19.93	45.36	13.42	—
K	9.99	21.85	44.63	8.53	15.00

Figure S1. Locations of municipal solid waste incineration facilities for collection of fly ash samples. I: Shanghai city (A, B, H, J, and K samples); II: Guangxi province sample (C); III: Zhejiang (D); IV: Shandong province (E, F, G, and I samples).

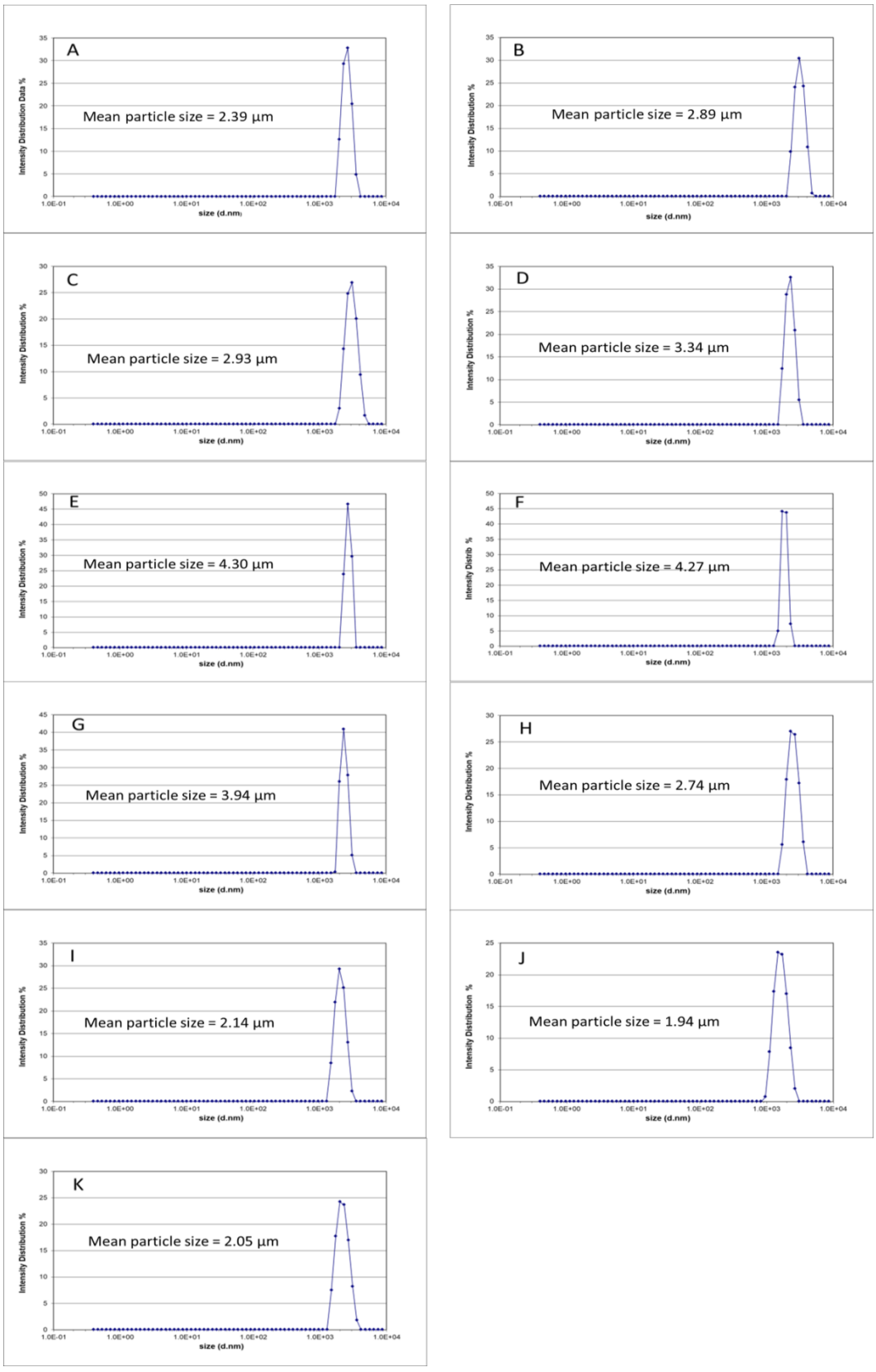


Figure S2 Particle size distribution of fly ash from municipal solid waste incinerators.

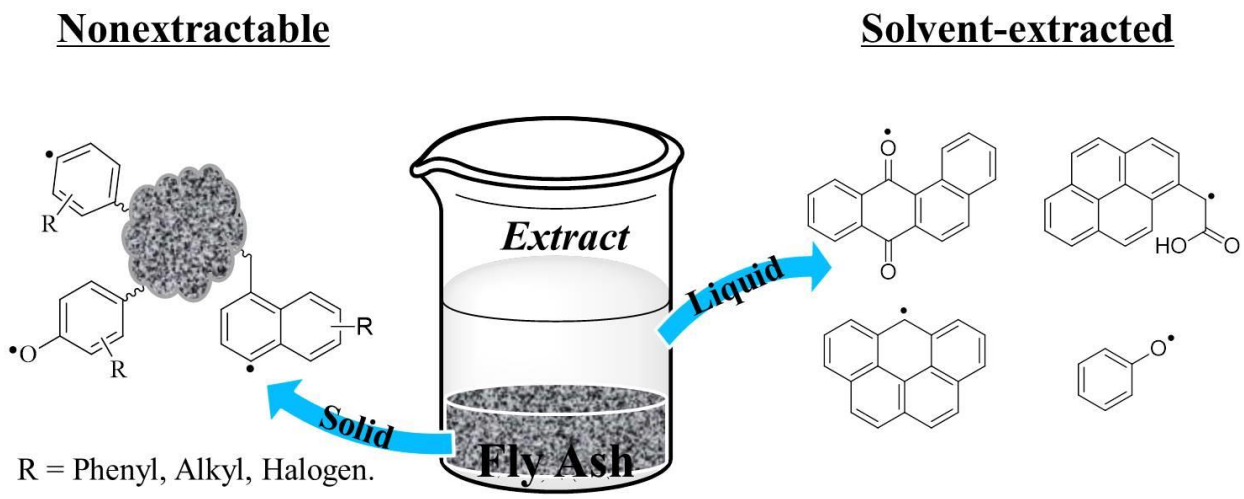


Figure S3. Conceptual diagram of solvent-extracted and non-extractable EPFRs on fly ash samples.

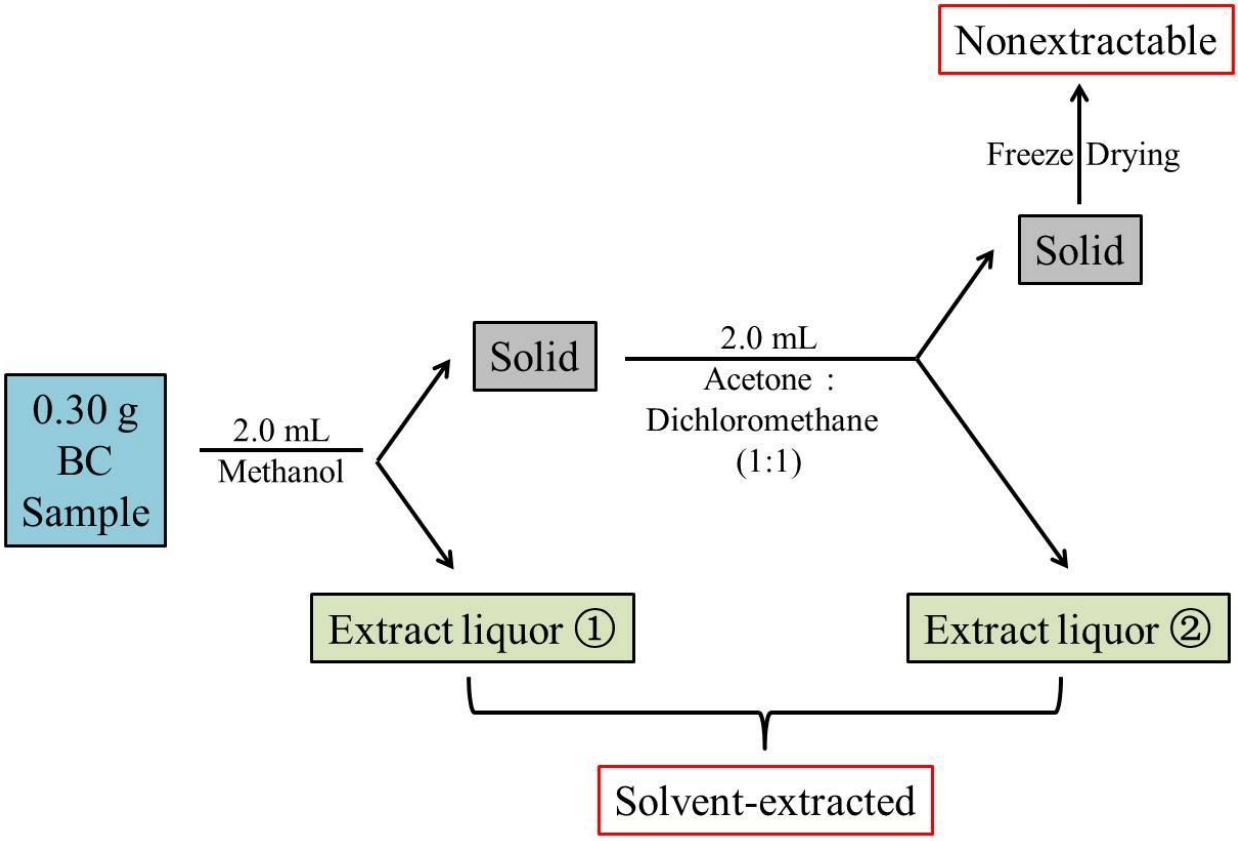


Figure S4. Scheme of the processes involved in obtaining solvent-extracted and nonextractable fly ash samples.

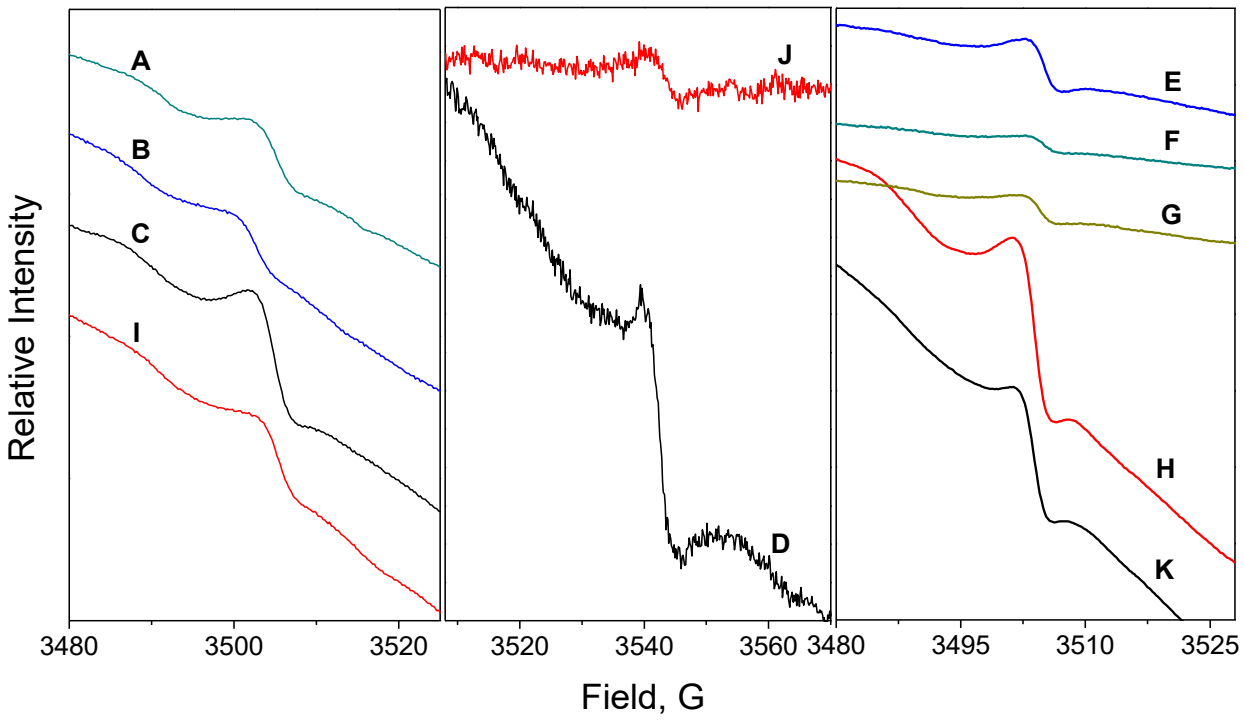


Figure S5. EPR spectra of different original samples at room temperature.

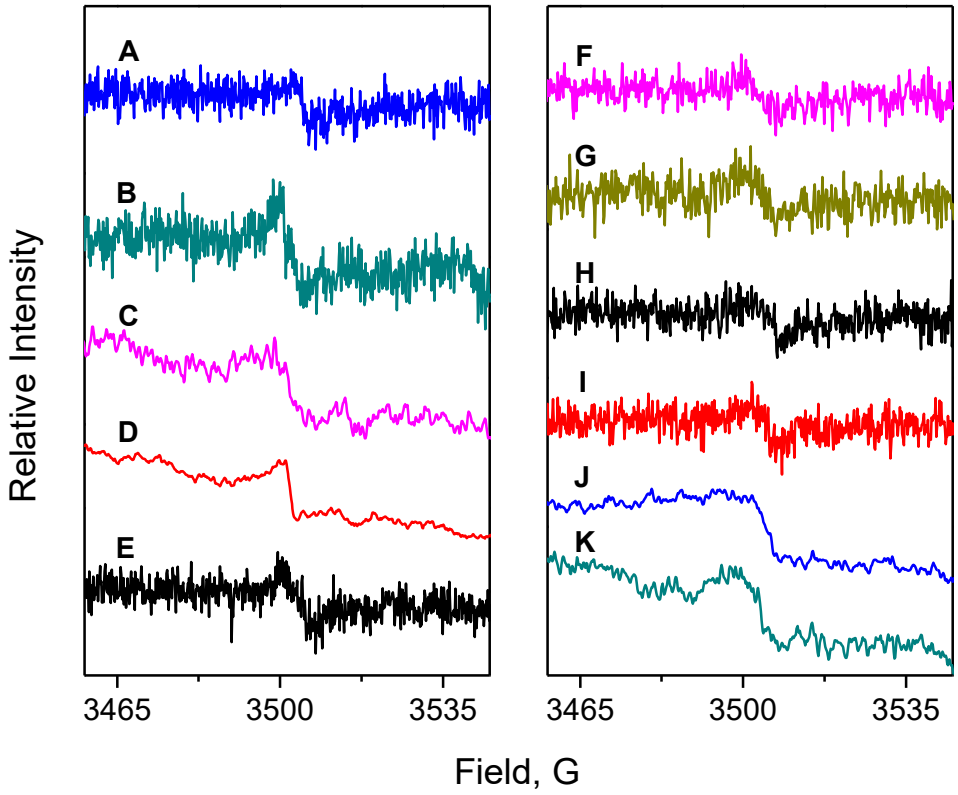


Figure S6. EPR spectra of different nonextractable samples of fly ash at room temperature.

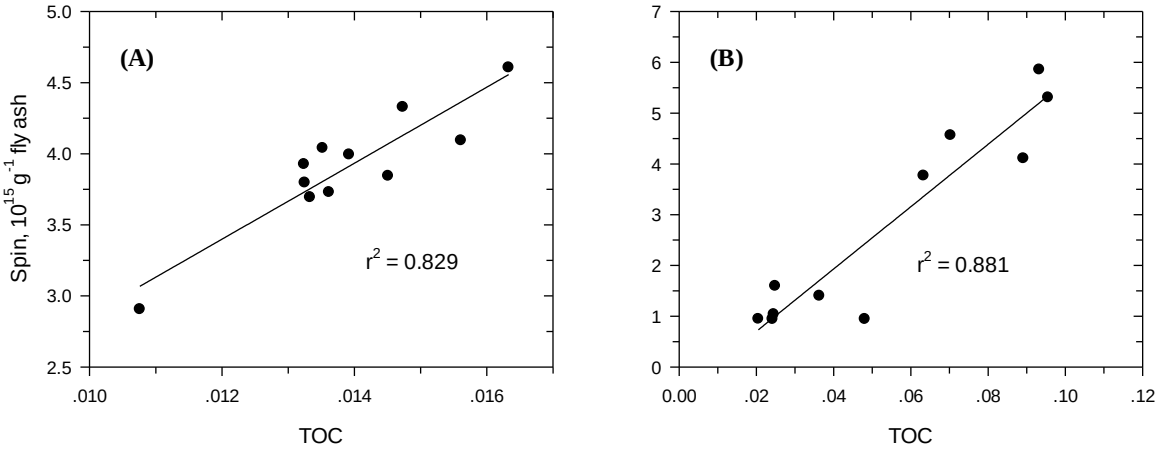


Figure S7. Concentrations of EPFRs versus TOC of solvent-extracted (A) and nonextractable (B) samples collected at different municipal solid waste incineration facilities in China.

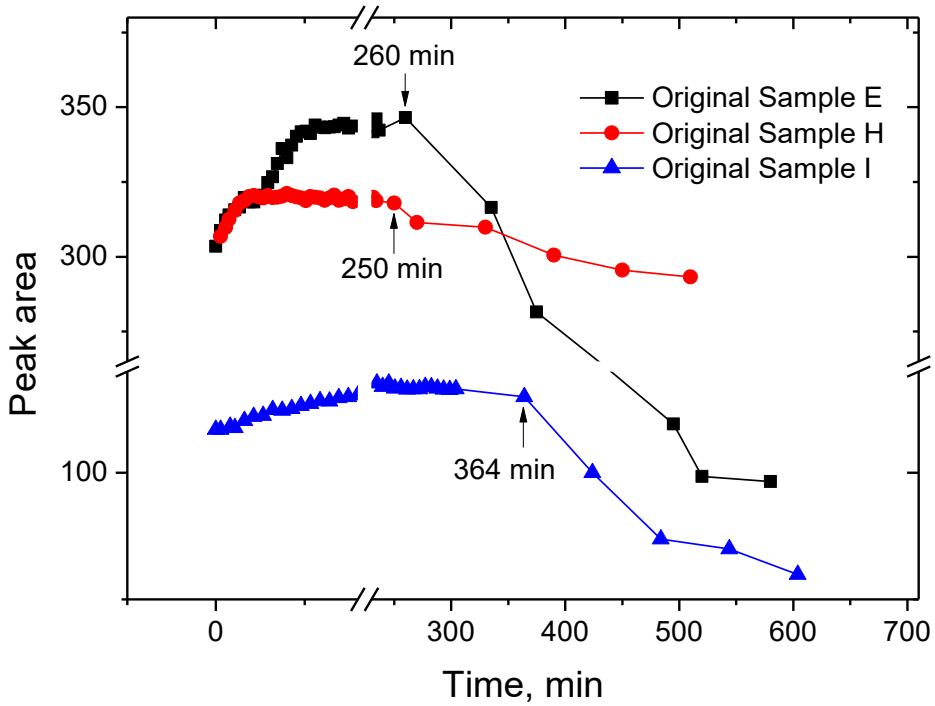


Figure S8. Evolution of EPFRs characteristics over a prolong irradiation time.

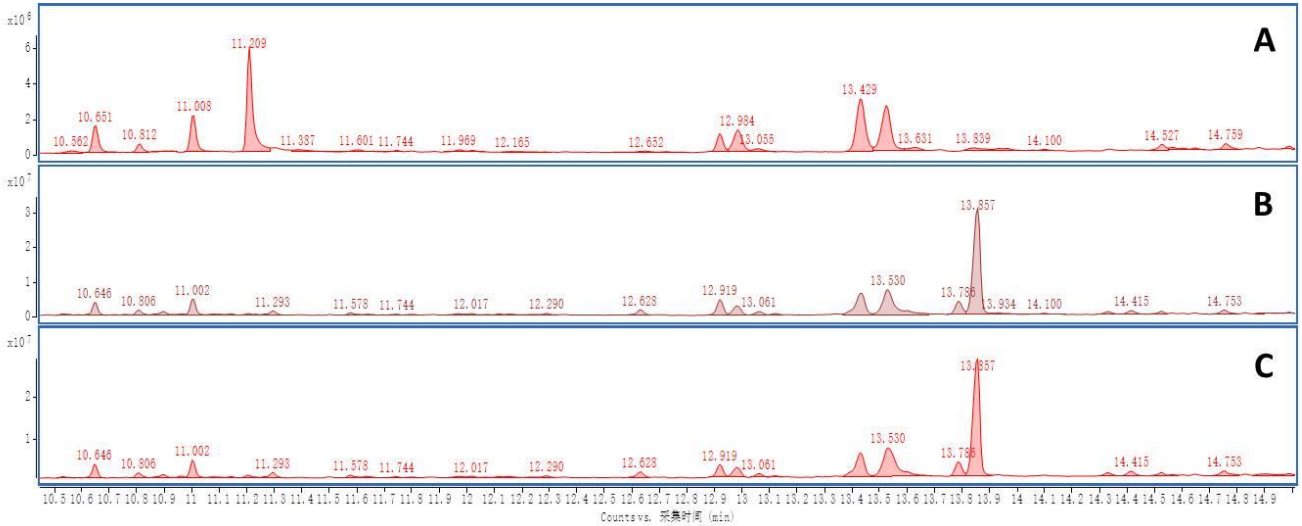
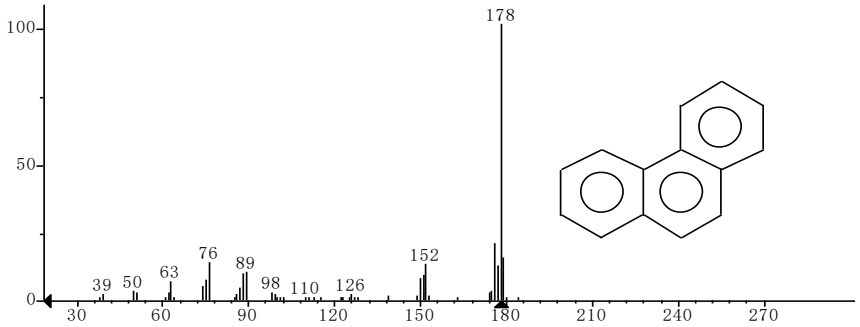
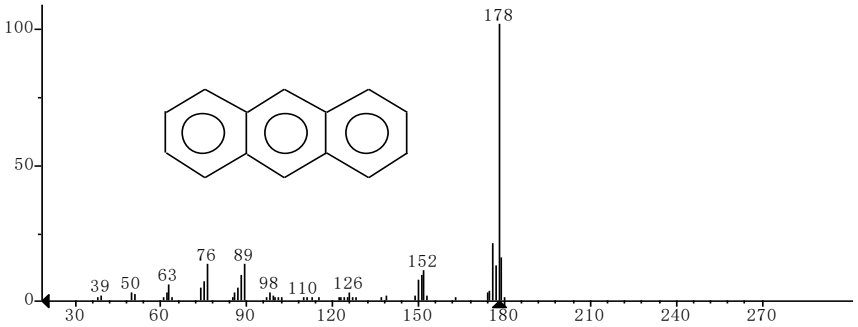


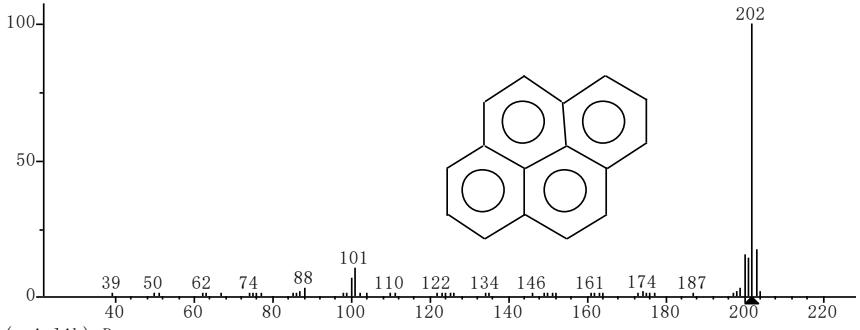
Figure S9. GC-MS chromatograms of original fly ash samples collected at different municipal solid waste incineration facilities in China. A-0 min; B-150 min; C-400min.



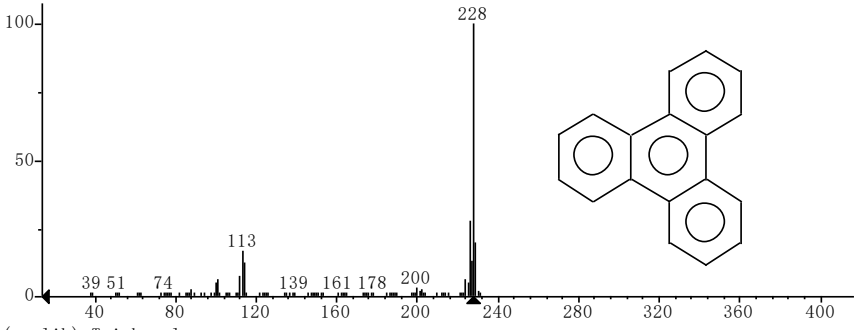
(mainlib) Phenanthrene



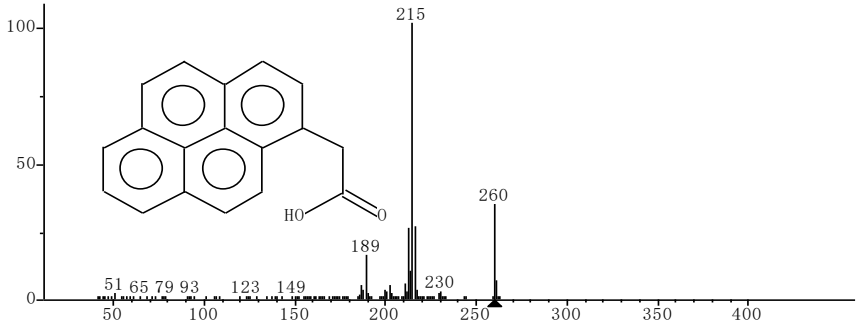
(replib) Anthracene



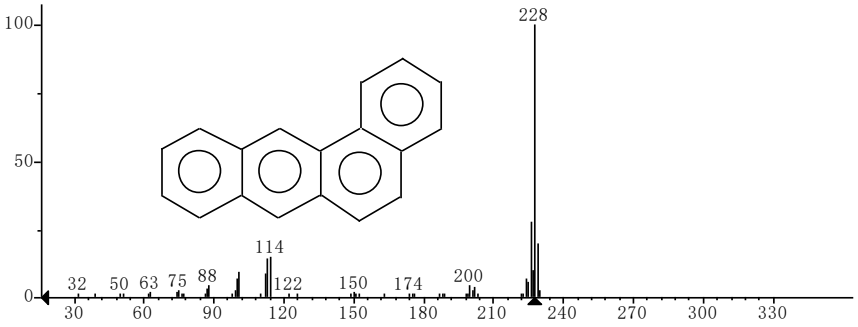
(mainlib) Pyrene



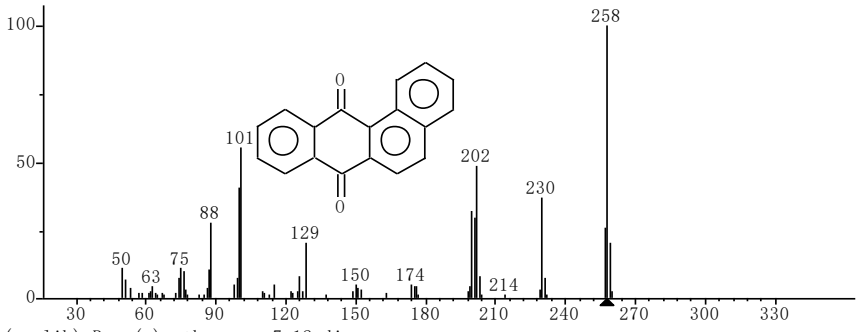
(replib) Triphenylene



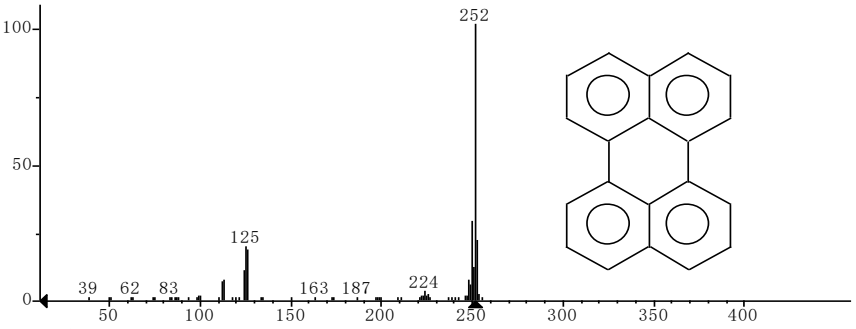
(mainlib) 3-Pyrenylacetic acid



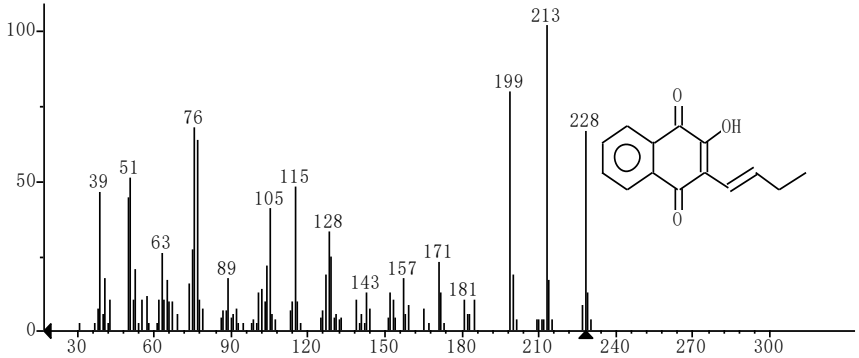
(mainlib) Benz[a]anthracene

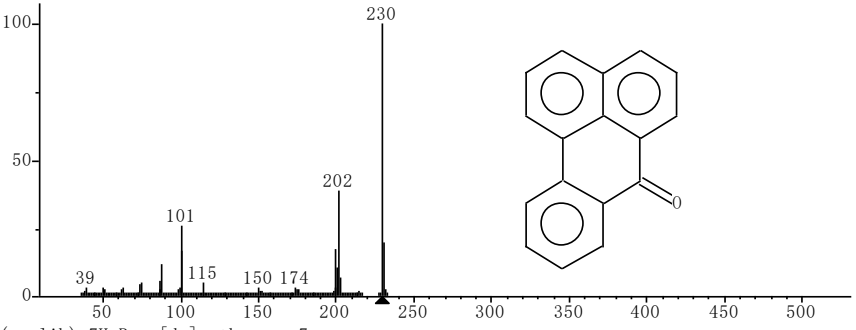


(replib) Benz(a)anthracene-7,12-dione

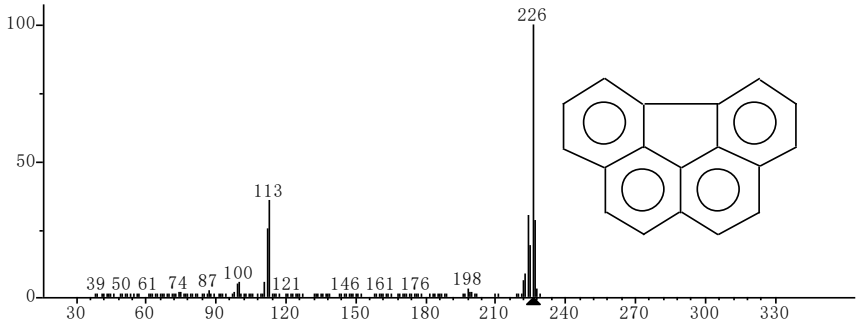


(replib) Perylene

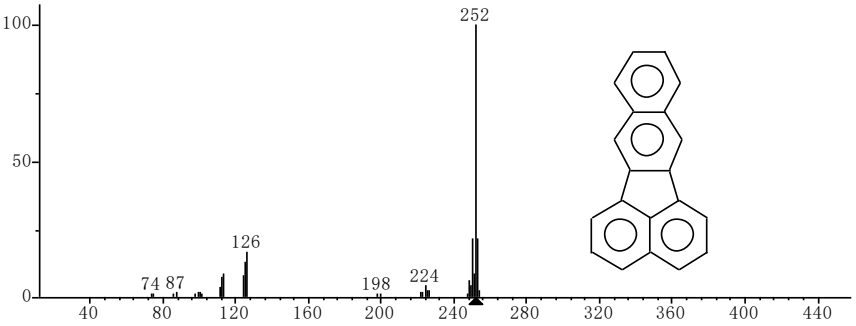




(replib) 7H-Benz[de]anthracen-7-one



(mainlib) Benzo[ghi]fluoranthene



(mainlib) Benzo[k]fluoranthene

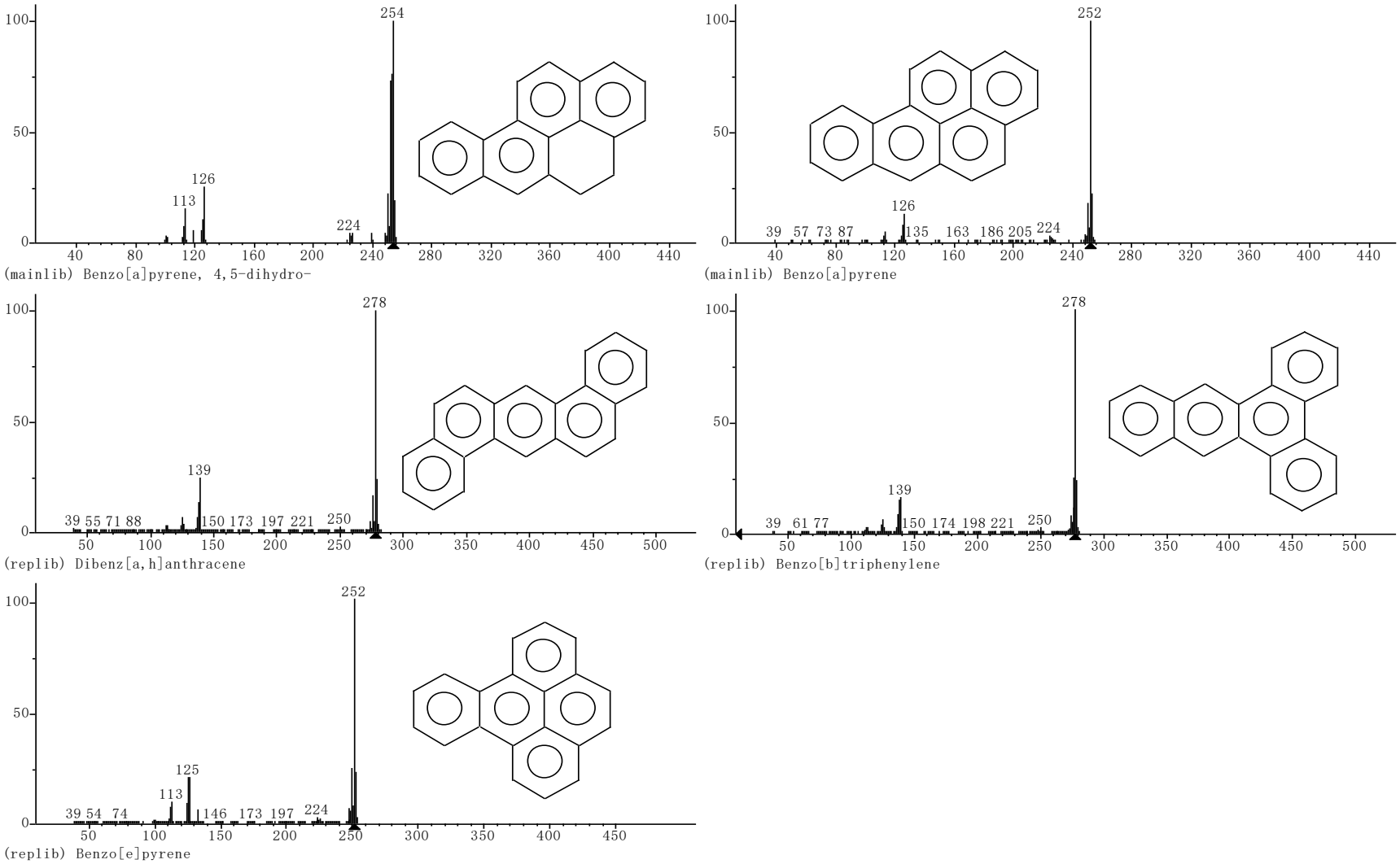


Figure S10. GC-MS chromatograms obtained after the photochemical process for original and nonextractable samples of fly ash.

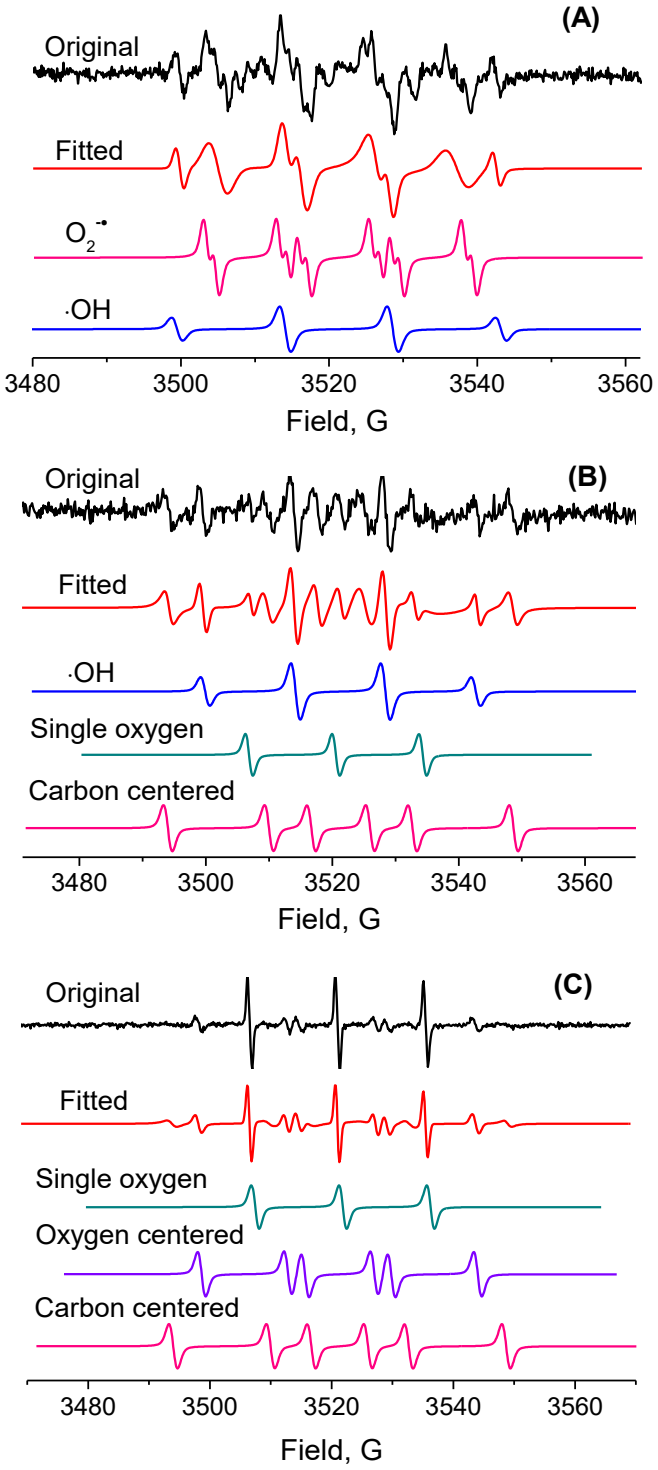


Figure S11. EPRs spectra of radical species obtained for solvent-extracted and nonextractable samples of fly ash. [(A) original sample A in DMPO+DMSO. (B) A and (C) K samples in DMPO+H_2O]