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Supplement of

Heterogeneous phototransformation of halogenated polycyclic aromatic hydrocarbons: influencing factors, mechanisms and products

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S1. Information on simulation experiments

Particle simulation in the laboratory was conducted as follows: Silica particles were suspended in toluene solvent at a concentration of 50 mg/mL. Subsequently, 200 μL of this suspension was deposited onto the surface of a circular quartz reactor with a diameter of 10 mm. The substrate was then dried in an oven set at 60 ℃ for 15 min, ensuring the formation of a uniform layer of silica particles at the bottom of the vessel.

The entire photolysis reaction unit comprises a gas supply, mass flowmeters, a dryer (with molecular sieve and color silica gel), a bubbler containing Milli-Q water, a xenon lamp, an optical reactor, a quartz reaction vessel, a temperature control system, gas absorption bottles, and a relative humidity monitoring component. Synthetic pure air is introduced into the reactor via channels equipped with switch valves and mass flowmeters. The air then passes through a dryer containing a molecular sieve and colored silica gel before being bubbled through Milli-Q water (H_2O) to produce dry air, moist air, and air containing hydrogen peroxide.

The optical reactor consists of a photochemical reaction vessel (GXAS-10, manufactured by China NBeT Group Corp), comprising a quartz reaction vessel, cover, and high-intensity transmittance quartz wafer (transmitting light in the range of 20-2,500 nm with over 95% efficiency). Flange-sealed connections and silica gel rings ensure the air tightness of the reaction chamber, with quartz reaction vessels positioned within the reactor. Solar-simulated irradiation is achieved using a xenon lamp (CEM-500, manufactured by China NBeT Group Corp) with an AM1.5 filter, providing a spectrum closely resembling sunlight. All experiments are conducted under a constant irradiation intensity of 100 mW/cm^{-2}. This was identified as the strongest intensity for the sampling sites at noon, and also applied in previous studies.[1]

Temperature control (298±0.5 K) is maintained using a low-temperature circulation chiller (CC-2005E, manufactured by Shenzhen Leputo Instrument Technology Co., LTD), which circulates condensed water around the outer sandwich of the reactor. An online hygrothermograph at the reactor outlet monitors temperature and humidity. Finally, the reacted gas is passed into a toluene solution to collect the tail gas. The absorbed toluene solution was analyzed for XPAHs to investigate the volatilization contributions. And less than 1% of XPAHs could be found in the absorbed toluene, thus ignored in the following discussion.

In the investigation of XPAH transformation mechanisms over time, the reactor temperature was maintained at 15°C, humidity at 45%, and no H_2O_2 was added. Various time points (0 min, 10 min, 30 min, 60 min, and 180 min) were examined. When exploring the influence of humidity, the photo exposure duration was set to 1 h, the temperature to 15°C, and no H_2O_2 was added. Humidity levels of 30%, 45%, and 60% were investigated. In the examination of temperature effects, the photo exposure duration was 1 h, humidity was controlled at 45%, and no H_2O_2 was added. Temperatures of 10°C, 15°C, 20°C, and 30°C were examined. When studying the impact of H_2O_2 levels on XPAHs transformation, the light exposure duration was 1 h, humidity was controlled at 45%, temperature was 15°C, and H_2O_2 levels of 0% (with TBA added), 0%, 1%, 3%, 5%, and 10% were examined. Dark control experiments were conducted for all photo exposure experiments. Humidity was controlled by adjusting the gas flow rate and the water level in the absorption bottle, and it was monitored by a sensor throughout the experiments. The temperature was regulated by a water bath surrounding the reactor.

[1] Qiuyue Zhang, Yu Wang*, Meng Gao, Yongcheng Li, Leicheng Zhao, Yiming Yao, Hao Chen, Lei Wang, and Hongwen Sun*, Organophosphite Antioxidants and Novel Organophosphate Esters in Dust from China: Large-Scale Distribution and Heterogeneous Phototransformation, Environmental Science & Technology 2023, 57, 10, 4187-4198

S2. Information on non-target analysis

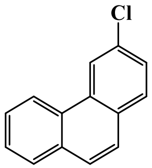
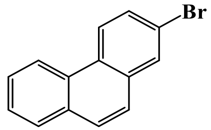
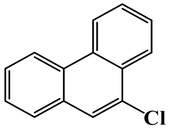
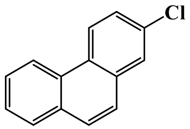
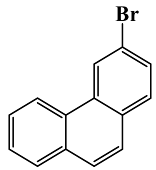
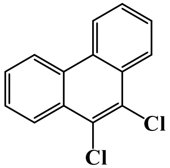
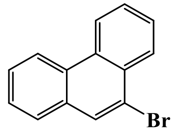
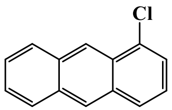
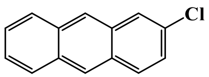
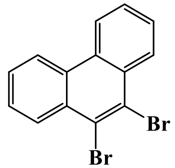
In the non-target analysis, separation was conducted on a DB-5 MS column (60 m × 0.25 μm × 0.25 mm, Agilent Technologies, USA). The oven temperature program was set as follows: the initial temperature was 50 ℃ (held for 1 min), increased to 280 ℃ at 10 ℃/min, then increased to 310 ℃ at 10 ℃/min and held for 5 min. The mass resolution was set at 60,000 FWHM at m/z 200. The maximum injection time was 200 ms, and the mass tolerance window was set to ± 5 ppm. Deconvolution parameters were set as follows: minimum intensity signals, 1e7; mass error (MS), ± 5 ppm; signal-to-noise ratio, 3; ion overlap window, 99; RT alignment, 10 sec.

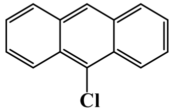
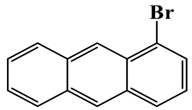
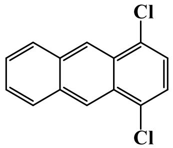
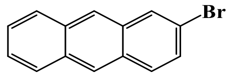
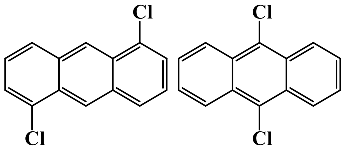
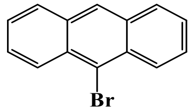
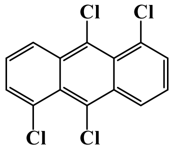
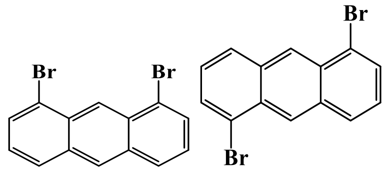
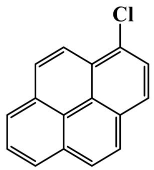
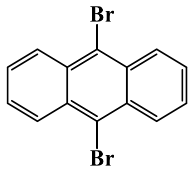
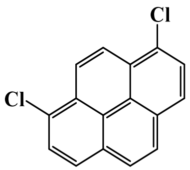
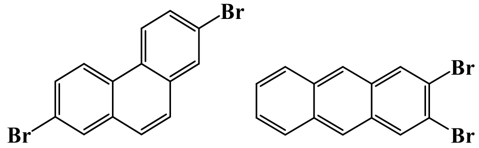
S3. Influence of particulate matter particle size

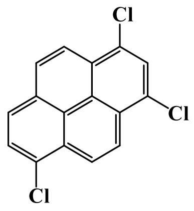
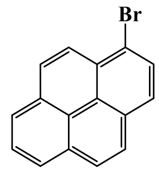
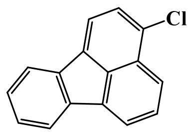
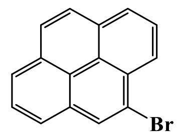
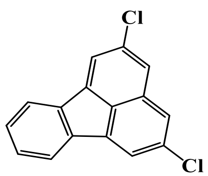
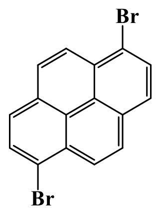
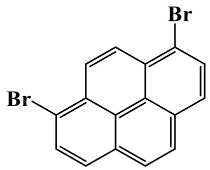
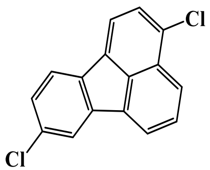
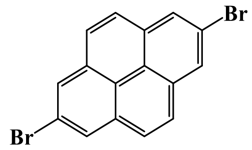
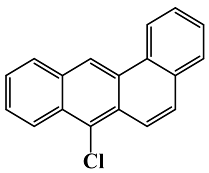
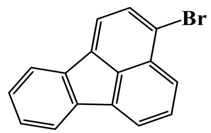
The variation in degradation rates caused by different particle sizes is not significant. A slight increase in the degradation rate is observed as the particle size increases, indicating that larger particles provide a greater surface area for adsorption, thereby resulting in a marginally higher degree of degradation. However, the overall impact of particle size variation is negligible. Consequently, a uniform particle size of 2 μm will be adopted for subsequent investigations.

Table S1.

Detailed information on 41 XPAHs.

Name	abbreviation	Molecular structures	Name	abbreviation	molecular structures
3-Chlorophenanthrene	3-ClPhe		2-Bromophenanthrene	2-BrPhe	
9-Chlorophenanthrene/ 2-Chlorophenanthrene	9-ClPhe/ 2-ClPhe	 	3-Bromophenanthrene	3-BrPhe	
9,10-Dichlorophenanthrene	9,10-Cl_2Phe		9-Bromophenanthrene	9-BrPhe	
1-Chloroanthracene/ 2-Chloroanthracene	1-ClAnt/ 2-ClAnt	 	9,10-Dibromophenanthrene	9,10-Br_2Phe	

9-Chloroanthracene	9-ClAnt		1-Bromoanthracene	1-BrAnt	
1,4-Dichloroanthracene	1,4-Cl_2Ant		2-Bromoanthracene	2-BrAnt	
1,5-Dichloroanthracene/ 9,10-dichloroanthracene	1,5-Cl_2Ant/ 9,10-Cl_2Ant		9-Bromoanthracene	9-BrAnt	
1,5,9,10-Tetrachloroanthracene	1,5,9,10-Cl_4Ant		1,8-Dibromoanthracene/ 1,5-dibromoanthracene	1,8-Br_2Ant/ 1,5-Br_2Ant	
1-Chloropyrene	1-ClPyr		9,10-Dibromoanthracene	9,10-Br_2Ant	
1,8-Dichloropyrene	1,8-Cl_2Pyr		2,7-Dibromophenanthrene/ 2,3-Dibromoanthracene	2,7-Br_2Phe/ 2,3-Br_2Ant	

1,3,6-Trichloropyrene	1,3,6-Cl_3Pyr		1-Bromopyrene	1-BrPyr	
3-Chlorofluoranthene	3-ClFluor		4-Bromopyrene	4-BrPyr	
2,5-Dichlorofluoranthene	2,5-Cl_2Fluor		1,6-Dibromopyrene/ 1,8-dibromopyrene	1,6-Br_2Pyr/ 1,8-Br_2Pyr	 
3,8-Dichlorofluoranthene	3,8-Cl_2Fluor		2,7-Dibromopyrene	2,7-Br_2Pyr	
7-Chlorobenz[a]anthracene	7-ClBaA		3-Bromofluoranthrene	3-BrFluor	

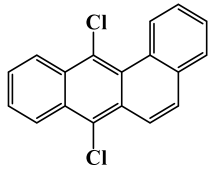
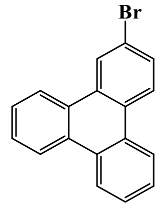
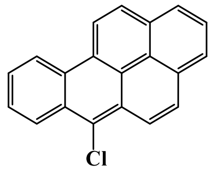
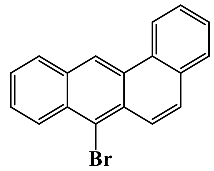
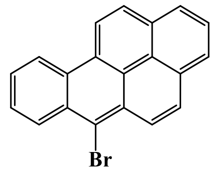
7,12-Dichlorobenz[a]anthracene	7,12-Cl_2BaA		2-Bromotriphenylene	2-BrTriph	
6-Chlorobenzo[a]pyrene	6-ClBaP		7-Bromobenz[a]anthracene	7-BrBaA	
			6-Bromobenzo[a]pyrene	6-BrBaP	

Table S2.

Seasonal distributions of ClPAHs and their congeners classified according to parent PAHs.

		Spring (fg/m^3)	Summer (fg/m^3)	Autumn (fg/m^3)	Winter (fg/m^3)	
	3-ClPhe	77.8	N.D.	62.4	757.8	
ClPhe	**9-ClPhe/2-ClPhe**	211.4	379.6	221.6	652.7	
	9,10-Cl_2Phe	150.9	91.1	120.8	180.0	
	sum	**440.1**	**470.7**	**404.8**	**1590.5**	**2906.1**
	1-ClAnt/2-ClAnt	28.6	131.4	148.4	615.548	
	9-ClAnt	20.9	170.4	180.0	198.0	
ClAnt	**1,4-Cl_2Ant**	27.8	N.D.	84.2	277.4	
	1,5-Cl_2Ant/9,10-Cl_2Ant	191.0	135.9	385.3	902.4	
	1,5,9,10-Cl_4Ant	78.3	N.D.	99.0	N.D.	
	sum	**346.6**	**437.7**	**896.9**	**1993.3**	**3674.5**
	1-ClPyr	326.1	837.1	378.4	1436.9	
	1,8-Cl_2Pyr	16.1	N.D.	49.1	113.2	
ClPyr	**1,3,6-Cl_3Pyr**	102.3	N.D.	160.4	86.0	
	sum	**444.5**	**837.1**	**587.9**	**1636.1**	**3505.6**
	3-ClFluor	132.3	747.5	166.1	919.7	
ClFluor	**2,5-Cl_2Fluor**	1084.7	N.D.	105.7	837.6	
	3,8-Cl_2Fluor	1091.7	N.D.	147.0	879.1	
	sum	**2308.7**	**747.5**	**418.8**	**2636.4**	**6111.4**
ClBaA	**7-ClBaA**	51.2	178.3	49.9	62.0	
	7,12-Cl_2BaA	5.7	N.D.	N.D.	1.8	
	sum	**56.9**	**178.3**	**49.9**	**63.8**	**348.9**
ClBaP	**6-ClBaP**	507.8	1726.1	570.5	2551.9	**5356.3**

Table S3.

Seasonal distributions of BrPAHs and their congeners classified according to parent PAHs.

		Spring (fg/m^3)	Summer (fg/m^3)	Autumn (fg/m^3)	Winter (fg/m^3)	
BrPhe	**2-BrPhe**	95.13	N.D.	N.D.	87.66	
	3-BrPhe	N.D.	N.D.	9.07	N.D.	
	9-BrPhe	104.76	N.D.	N.D.	139.94	
	9,10-Br_2Phe	45.75	N.D.	24.03	29.96	
	sum	**245.64**	**N.D.**	**33.10**	**257.56**	**536.30**
BrAnt	**1-BrAnt**	N.D.	N.D.	N.D.	N.D.	
	9-BrAnt	49.03	N.D.	N.D.	10.01	
	1,8-Br_2Ant/1,5-Br_2Ant	27.14	N.D.	2.51	84.80	
	9,10-Br_2Ant	27.17	N.D.	27.20	226.15	
	sum	**103.34**	**N.D.**	**29.71**	**320.96**	**454.01**
BrPyr	**1-BrPyr**	14.47	N.D.	N.D.	718.71	
	4-BrPyr	18.74	N.D.	N.D.	767.08	
	1,6-Br_2Pyr	107.79	N.D.	25.28	34.57	
	sum	**141.00**	**N.D.**	**25.28**	**1520.36**	**1686.63**
BrFluor	**3-BrFluor**	N.D.	N.D.	N.D.	N.D.	**N.D.**
BrTriph	**2-BrTriph**	30.95	N.D.	115.13	N.D.	**146.08**
BrBaA	**7-BrBaA**	36.79	N.D.	51.18	N.D.	**88.66**

Table S4.

The concentrations (pg/m^3) and distributions of individual XPAHs on particulate matter.

	3/22/2023-4/6/2023	**4/7/2023-4/12/2023**	**4/29/2023-5/14/2023**	**6/18/2023-7/2/2023**	**8/18/2023-8/30/2023**	**9/25/2023-10/10/2023**	**10/11/2023-10/30/2023**	**11/18/2023-11/26/2023**	**12/4/2023-12/11/2023**	**12/26/2023-1/12/2024**	**1/12/2024-1/22/2024**	**Average (%)**
2,7-Cl_2Fle	N.D.	N.D.	N.D.	1930.3	107.3	198.8	145.2	137.3	N.D.	N.D.	N.D.	1.3%
	0.0%	**0.0%**	**0.0%**	**3.1%**	**3.0%**	**4.3%**	**0.7%**	**3.0%**	**0.0%**	**0.0%**	**0.0%**	
3-ClPhe	1084.6	59.1	25.5	2230.8	130.0	N.D.	1381.4	101.8	3.3	81.9	17.0	2.3%
	5.0%	**1.1%**	**0.5%**	**3.6%**	**3.6%**	**0.0%**	**6.3%**	**2.2%**	**0.5%**	**2.2%**	**0.5%**	
9-ClPhe/2-ClPhe	1177.8	569.5	95.1	3876.4	327.7	379.6	2373.7	163.8	42.0	458.9	210.7	7.4%
	5.4%	**11.0%**	**2.0%**	**6.3%**	**9.0%**	**8.3%**	**10.8%**	**3.6%**	**6.6%**	**12.2%**	**6.0%**	
9,10-Cl_2Phe	399.6	127.0	N.D.	1927.8	301.8	91.1	1205.4	360.5	2.0	N.D.	13.5	2.9%
	1.8%	**2.5%**	**0.0%**	**3.1%**	**8.3%**	**2.0%**	**5.5%**	**7.9%**	**0.3%**	**0.0%**	**0.4%**	
1-ClAnt/2-ClAnt	1738.0	90.2	12.6	861.9	44.6	131.4	253.8	156.8	1.0	287.5	18.4	2.6%
	8.0%	**1.7%**	**0.3%**	**1.4%**	**1.2%**	**2.9%**	**1.2%**	**3.5%**	**0.2%**	**7.7%**	**0.5%**	
9-ClAnt	521.4	55.8	12.1	2791.0	29.7	170.4	321.3	440.1	100.0	N.D.	16.8	3.7%
	2.4%	**1.1%**	**0.3%**	**4.5%**	**0.8%**	**3.7%**	**1.5%**	**9.7%**	**15.7%**	**0.0%**	**0.5%**	
1,4-Cl_2Ant	768.8	63.3	N.D.	1803.9	55.6	N.D.	629.2	252.5	N.D.	N.D.	N.D.	1.6%
	3.6%	**1.2%**	**0.0%**	**2.9%**	**1.5%**	**0.0%**	**2.9%**	**5.6%**	**0.0%**	**0.0%**	**0.0%**	
1,5-Cl_2Ant/9,10-Cl_2Ant	2391.1	221.5	59.4	3896.7	322.5	135.9	2094.5	1004.6	151.4	N.D.	94.5	8.5%
	11.1%	**4.3%**	**1.3%**	**6.3%**	**8.9%**	**3.0%**	**9.5%**	**22.2%**	**23.8%**	**0.0%**	**2.7%**	
1,5,9,10-Cl_4Ant	N.D.	N.D.	8.9	2103.5	147.6	N.D.	23.0	297.1	N.D.	N.D.	N.D.	1.3%
	0.0%	**0.0%**	**0.2%**	**3.4%**	**4.1%**	**0.0%**	**0.1%**	**6.6%**	**0.0%**	**0.0%**	**0.0%**	
1-ClPyr	3362.2	641.9	260.9	2096.0	391.3	837.1	457.8	321.9	94.5	718.6	306.6	10.7%
	15.6%	**12.4%**	**5.6%**	**3.4%**	**10.8%**	**18.2%**	**2.1%**	**7.1%**	**14.8%**	**19.2%**	**8.7%**	
1,8-Cl_2Pyr	258.4	54.5	N.D.	2135.2	32.3	N.D.	697.0	85.7	7.5	54.0	26.7	1.4%

	1.2%	**1.1%**	**0.0%**	**3.5%**	**0.9%**	**0.0%**	**3.2%**	**1.9%**	**1.2%**	**1.4%**	**0.8%**	
1,3,6-Cl_3Pyr	N.D.	194.3	N.D.	2159.3	204.5	N.D.	995.3	274.8	16.4	190.1	63.6	3.0%
	0.0%	**3.8%**	**0.0%**	**3.5%**	**5.6%**	**0.0%**	**4.5%**	**6.1%**	**2.6%**	**5.1%**	**1.8%**	
3-ClFluor	1979.8	436.3	103.3	14487.8	161.4	747.5	6546.8	N.D.	17.2	481.2	343.0	10.8%
	9.2%	**8.4%**	**2.2%**	**23.6%**	**4.4%**	**16.3%**	**29.8%**	**0.0%**	**2.7%**	**12.8%**	**9.8%**	
2,5-Cl_2Fluor	1403.7	363.1	1751.5	2294.2	417.8	N.D.	1887.1	317.0	N.D.	N.D.	745.9	9.4%
	6.5%	**7.0%**	**37.3%**	**3.7%**	**11.5%**	**0.0%**	**8.6%**	**7.0%**	**0.0%**	**0.0%**	**21.3%**	
3,8-Cl_2Fluor	1403.7	367.4	1717.8	2556.9	465.6	N.D.	2103.2	408.4	N.D.	32.6	866.3	10.1%
	6.5%	**7.1%**	**36.6%**	**4.2%**	**12.8%**	**0.0%**	**9.6%**	**9.0%**	**0.0%**	**0.9%**	**24.7%**	
7-ClBaA	N.D.	116.8	42.8	N.D.	59.6	178.3	28.4	N.D.	16.0	133.7	69.3	1.5%
	0.0%	**2.3%**	**0.9%**	**0.0%**	**1.6%**	**3.9%**	**0.1%**	**0.0%**	**2.5%**	**3.6%**	**2.0%**	
7,12-Cl_2BaA	N.D.	5.4	17.2	11681.9	N.D.	N.D.	720.3	N.D.	N.D.	N.D.	N.D.	2.1%
	0.0%	**0.1%**	**0.4%**	**19.0%**	**0.0%**	**0.0%**	**3.3%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
6-ClBaP	5129.7	1809.8	586.9	2626.7	428.7	1726.1	78.8	212.7	185.5	1313.4	716.2	19.5%
	23.7%	**35.0%**	**12.5%**	**4.3%**	**11.8%**	**37.6%**	**0.4%**	**4.7%**	**29.1%**	**35.0%**	**20.4%**	
5-BrAna	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
2-BrFle	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
2,7-Br_2Fle	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
2-BrPhe	N.D.	236.6	N.D.	N.D.	285.4	N.D.	N.D.	N.D.	N.D.	N.D.	26.4	6.4%
	0.0%	**31.0%**	**0.0%**	**0.0%**	**21.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**18.6%**	
3-BrPhe	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	27.2	N.D.	0.5%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**5.1%**	**0.0%**	
9-BrPhe	203.6	191.4	N.D.	N.D.	314.3	N.D.	N.D.	N.D.	N.D.	N.D.	24.8	6.3%

	3.8%	**25.1%**	**0.0%**	**0.0%**	**23.1%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**17.5%**	
9,10-Br_2Phe	N.D.	61.3	100.0	N.D.	37.3	N.D.	N.D.	N.D.	N.D.	79.8	10.1	3.8%
	0.0%	**8.0%**	**9.4%**	**0.0%**	**2.7%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**14.9%**	**7.1%**	
1-BrAnt	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
9-BrAnt	30.0	N.D.	N.D.	N.D.	147.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.0%
	0.6%	**0.0%**	**0.0%**	**0.0%**	**10.8%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
1,8-Br_2Ant/1,5-Br_2Ant	206.1	48.3	N.D.	42.4	39.0	N.D.	N.D.	7.5	N.D.	N.D.	N.D.	6.9%
	3.8%	**6.3%**	**0.0%**	**61.7%**	**2.9%**	**0.0%**	**0.0%**	**1.5%**	**0.0%**	**0.0%**	**0.0%**	
9,10-Br_2Ant	628.2	50.2	75.3	N.D.	6.2	N.D.	N.D.	13.5	N.D.	68.1	N.D.	3.7%
	11.7%	**6.6%**	**7.1%**	**0.0%**	**0.5%**	**0.0%**	**0.0%**	**2.6%**	**0.0%**	**12.7%**	**0.0%**	
1-BrPyr	2066.6	89.5	N.D.	N.D.	43.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.8%
	38.4%	**11.7%**	**0.0%**	**0.0%**	**3.2%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
4-BrPyr	2244.8	56.5	N.D.	N.D.	56.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.8%
	41.7%	**7.4%**	**0.0%**	**0.0%**	**4.1%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
1,6-BrPyr	N.D.	29.6	711.8	26.3	185.2	N.D.	N.D.	26.4	N.D.	49.4	74.2	17.2%
	0.0%	**3.9%**	**66.9%**	**38.3%**	**13.6%**	**0.0%**	**0.0%**	**5.1%**	**0.0%**	**9.2%**	**52.3%**	
3-BrFluor	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.0%
	0.0%	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	
7-BrBaA	N.D.	N.D.	84.4	N.D.	247.9	N.D.	N.D.	236.0	23.7	200.9	6.3	19.4%
	0.0%	**0.0%**	**7.9%**	**0.0%**	**18.2%**	**0.0%**	**0.0%**	**45.6%**	**100.0%**	**37.5%**	**4.4%**	
2-BrTriph	N.D.	N.D.	92.8	N.D.	N.D.	N.D.	N.D.	234.5	N.D.	110.8	N.D.	6.8%
	0.0%	**0.0%**	**8.7%**	**0.0%**	**0.0%**	**0.0%**	**0.0%**	**45.3%**	**0.0%**	**20.7%**	**0.0%**	

Table S5. **Meteorological parameters during the sampling period.**

	Wind speed (m/s)	Wind direction (degree)	Air pressure (hpa)	Temperature (℃)	Humidity (%)	Irradiation (W/m^2)	Sunshine duration (h)	Rainfall (mm)
2023/3/22-2023/4/6	1.17	267.69	1013.74	22.91	67.38	330.25	12.40	45.74
2023/4/7-2023/4/12	1.03	208.00	1015.55	20.95	45.00	773.90	12.73	50.70
2023/4/29-2023/5/14	1.53	242.88	1010.13	24.05	55.13	591.79	13.47	75.01
2023/6/18-2023/7/2	1.45	266.80	1003.31	22.49	71.47	427.81	14.08	154.47
2023/8/18-2023/8/30	1.33	228.00	1003.71	30.41	65.15	592.79	13.10	284.58
2023/9/25-2023/10/10	1.11	243.81	1013.86	23.11	67.13	388.05	11.83	323.13
2023/10/11-2023/10/30	1.10	221.80	1016.87	28.02	53.45	577.81	11.30	324.60
2023/11/18-2023/11/26	1.02	214.89	1020.28	17.36	45.78	578.67	10.49	340.10
2023/12/4-2023/12/11	1.11	201.88	1014.44	16.44	56.50	399.95	10.26	340.70
2023/12/26-2024/1/12	0.88	179.61	1022.05	10.51	59.89	427.57	10.25	342.46
2024/1/12-2024/1/22	1.67	230.55	1024.22	10.19	65.18	310.67	10.43	344.44

Table S6.

The persistence (Pov), characteristic travel distance (CTD), transfer efficiency (TE), and the P-B LRTP assignment of XPAHs and their transformation products.

	Compound	Persistence (Pov)	Transfer Efficiency (TE)	Bioaccumulation Factor (BAF)	Characteristic Travel Distance (CTD)	LogPov	LogTE	LogBAF	P-B-LRTP Score
A	1,4-Cl_2Ant	171.25	0.20	3.97		2.23	-0.70	0.60	2.13
	Ant	164.28	0.01	2.60	132.43	2.22	-2.23	0.42	0.40
	1,4-Anthracenedione	105.61	1.97	1.32	519.26	2.02	0.29	0.12	2.44
	Naphthalene, 2-methyl-	37.61	0.00	2.21	101.89	1.58	-3.28	0.35	-1.36
	Nap	51.90	0.00	1.84	246.59	1.72	-2.45	0.27	-0.47
	Naphthalene, 1,2,3,4-tetrahydro-	23.47	0.00	1.97	155.28	1.37	-3.32	0.29	-1.65
	Phenol, 2-methoxy-	29.99	0.03	0.54	171.21	1.48	-1.47	-0.27	-0.27
	3-Nonanol	23.98	0.03	1.79	277.62	1.38	-1.50	0.25	0.13
	3-Nonanone	22.41	0.02	1.46	493.98	1.35	-1.65	0.16	-0.14
B	9,10-Cl_2Phe	748.84	33.96	4.63	8039.16	2.87	1.53	0.67	5.07
	Phe	634.89	0.06	3.27	398.48	2.80	-1.19	0.51	2.13
	9,10-Phenanthrenedione	94.78	0.35	1.33	93.35	1.98	-0.45	0.12	1.65
	Ethanone, 1-(4-methylphenyl)-	33.75	0.66	0.47	924.54	1.53	-0.18	-0.33	1.02
	[1,1'-Biphenyl]-2,2'-dicarboxylic acid	105.97	0.00	0.50	74.70	2.03	-2.41	-0.30	-0.68
	1,2-Benzenedicarboxylic acid	31.60	0.00	0.50	37.37	1.50	-2.47	-0.30	-1.27
	Dibutyl phthalate	24.96	0.28	2.64	505.44	1.40	-0.55	0.42	1.27
	9H-Fluoren-9-one	42.81	0.61	1.44	695.49	1.63	-0.22	0.16	1.57
	Benzophenone	42.13	1.31	1.18	1101.36	1.62	0.12	0.07	1.81
	3-Nonanone	22.41	0.02	1.46	493.98	1.35	-1.65	0.16	-0.14

C	1,8-Cl_2Pyr	/	/	/	/	/	/	/	/
	Pyr	169.73	0.01	2.89	124.14	2.23	-2.08	0.46	0.61
	Nap	51.90	0.00	1.84	246.59	1.72	-2.45	0.27	-0.47
	Naphthalene, 2-methyl-	37.61	0.00	2.21	101.89	1.58	-3.28	0.35	-1.36
	2,2'-Dimethylbiphenyl	385.47	0.02	2.87	617.62	2.59	-1.70	0.46	1.34
	4,4'-Dimethylbiphenyl	103.89	0.02	3.03	617.59	2.02	-1.70	0.48	0.79
	Benzophenone	42.13	1.31	1.18	1101.36	1.62	0.12	0.07	1.81
	Ethanone, 1-(4-methylphenyl)-	33.75	0.66	0.47	924.54	1.53	-0.18	-0.33	1.02
D	2,5-Cl_2Fluor	/	/	/	/	/	/	/	/
	2,7-Cl_2Fle	685.32	0.26	3.17	1048.93	2.84	-0.59	0.50	2.75
	9-ClFle	/	/	/	/	/	/	/	/
	4,4'-Dimethylbiphenyl	103.89	0.02	3.03	617.59	2.02	-1.70	0.48	0.79
	2,2'-Dimethylbiphenyl	102.38	0.02	2.87	617.61	2.01	-1.70	0.46	0.76
	Benzophenone	42.13	1.31	1.18	1101.36	1.62	0.12	0.07	1.81
	Fluor	171.28	0.17	3.07	450.23	2.23	-0.77	0.49	1.95
	1H-Indene, 2,3-dihydro-4,7-dimethyl-	65.85	0.00	2.68	247.11	1.82	-3.42	0.43	-1.17
	1H-Indene, octahydro-	18.84	0.00	2.11	309.47	1.28	-4.19	0.32	-2.59
	Nap	51.90	0.00	1.84	246.59	1.72	-2.45	0.27	-0.47
	Benzene, 1,2-diethyl-	22.90	0.00	2.12	657.35	1.36	-2.33	0.33	-0.65
	1,2-Benzenedicarboxylic acid	31.60	0.00	0.50	37.37	1.50	-2.47	-0.30	-1.27
	Dibutyl phthalate	24.96	0.28	2.64	505.44	1.40	-0.55	0.42	1.27
E	7,12-Cl_2BaA	/	/	/	/	/	/	/	/
	BaA	172.26	0.01	3.47	122.57	2.24	-2.07	0.54	0.71
	Benz(a)anthracene-7,12-dione	107.88	0.80	1.99	183.18	2.03	-0.10	0.30	2.23
	1,2-Benzenedicarboxylic acid	31.60	0.00	0.50	37.37	1.50	-2.47	-0.30	-1.27

	2,6-Diisopropylnaphthalene	105.21	0.00	3.68	80.59	2.02	-4.00	0.57	-1.41
	Dibutyl phthalate	24.96	0.28	2.64	505.44	1.40	-0.55	0.42	1.27
F	6-ClBaP	/	/	/	/	/	/	/	/
	BaP	172.94	0.04	3.71	162.38	2.24	-1.42	0.57	1.38
	Lapachol	42.53	0.00	1.15	37.37	1.63	-2.94	0.06	-1.25
	2,6-Diisopropylnaphthalene	105.21	0.00	3.68	80.59	2.02	-4.00	0.57	-1.41
	Mono(2-ethylhexyl) phthalate	43.25	1.22	0.50	369.12	1.64	0.09	-0.30	1.42
	Dibutyl phthalate	24.96	0.28	2.64	505.44	1.40	-0.55	0.42	1.27

Table S7.

The median lethal doses (LD50) and toxicity levels of XPAHs and their transformation products.

	Compound	Median lethal Dose LD50 (mg/kg)	Toxicity Level		Compound	Median lethal Dose LD50 (mg/kg)	Toxicity Level
A	1,4-Cl_2Ant	886	4	D	2,5-Cl_2Fluor	4220	5
	Ant	316	4		2,7-Cl_2Fle	6700	6
	1,4-Anthracenedione	190	3		9-ClFle	1070	4
	Naphthalene, 2-methyl-	1630	4		Benzophenone	2895	5
	Nap	316	4		Fluor	2000	4
	Naphthalene, 1,2,3,4-tetrahydro-	6700	6		1H-Indene, 2,3-dihydro-4,7-dimethyl-	2200	5
	Phenol, 2-methoxy-	520	4		1H-Indene, octahydro-	3660	5
	3-Nonanol	1000	4		Nap	316	4
	3-Nonanone	5000	5		Benzene, 1,2-diethyl-	2050	5
B	9,10-Cl_2Phe	886	4		1,2-Benzenedicarboxylic acid	2530	5
	Phe	316	4		Dibutyl phthalate	3474	5
	9,10-Phenanthrenedione	1500	4	E	7,12-Cl_2BaA	886	4
	Ethanone, 1-(4-methylphenyl)-	1320	4		BaA	316	4
	[1,1'-Biphenyl]-2,2'-dicarboxylic acid	2100	5		Benz(a)anthracene-7,12-dione	5000	5
	1,2-Benzenedicarboxylic acid	2530	5		1,2-Benzenedicarboxylic acid	2530	5
	Dibutyl phthalate	3474	5		2,6-Diisopropylnaphthalene	5300	6
	9H-Fluoren-9-one	1070	4		Dibutyl phthalate	3474	5
	Benzophenone	2895	5	F	6-ClBaP	886	4
	3-Nonanone	5000	5		BaP	316	4
C	1,8-Cl2Pyr	886	4		Lapachol	680	4
	Pyr	316	4		2,6-Diisopropylnaphthalene	5300	6

Nap	316	4	Mono(2-ethylhexyl) phthalate	1340	4
Naphthalene, 2-methyl-	1630	4	Dibutyl phthalate	3474	5
Benzophenone	2895	5			
Ethanone, 1-(4-methylphenyl)-	1320	4			

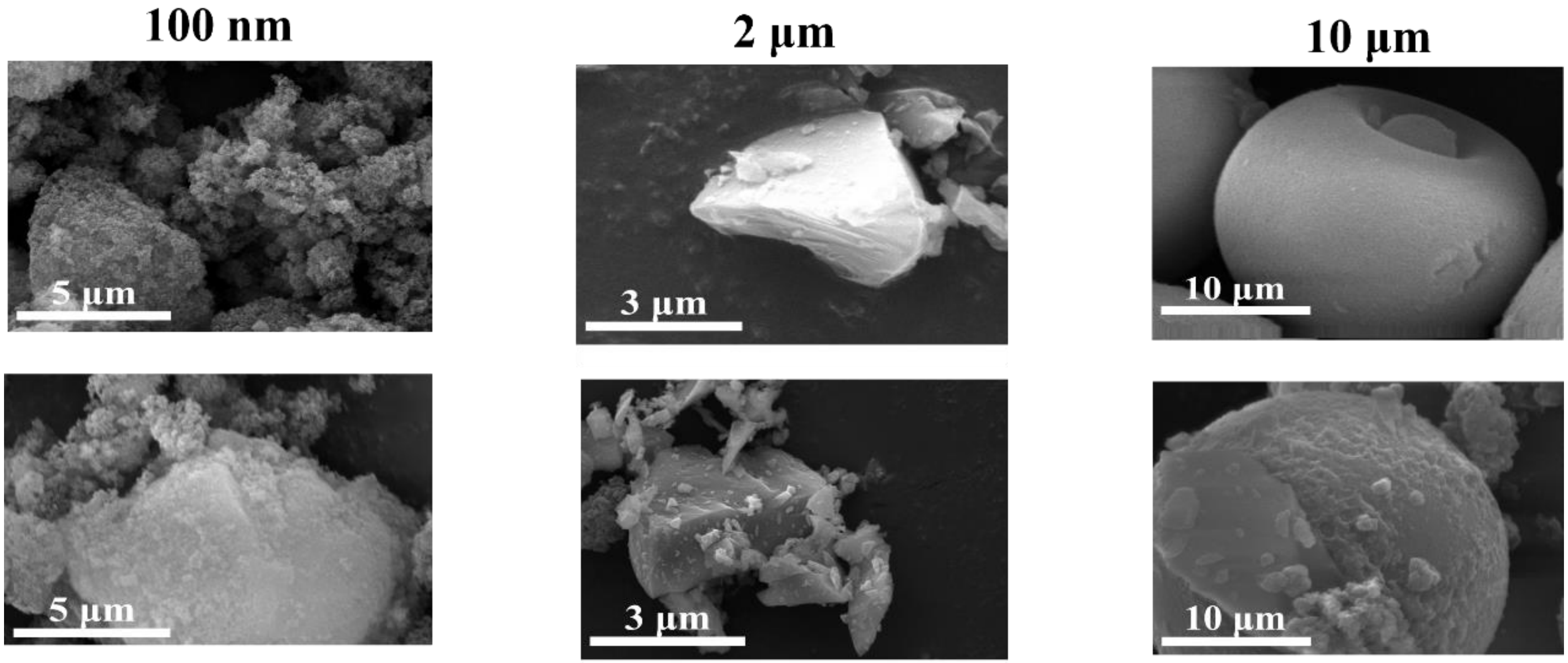


Fig. S1. Simulation of particulate loading conditions: Scanning electron microscopy (SEM) images.

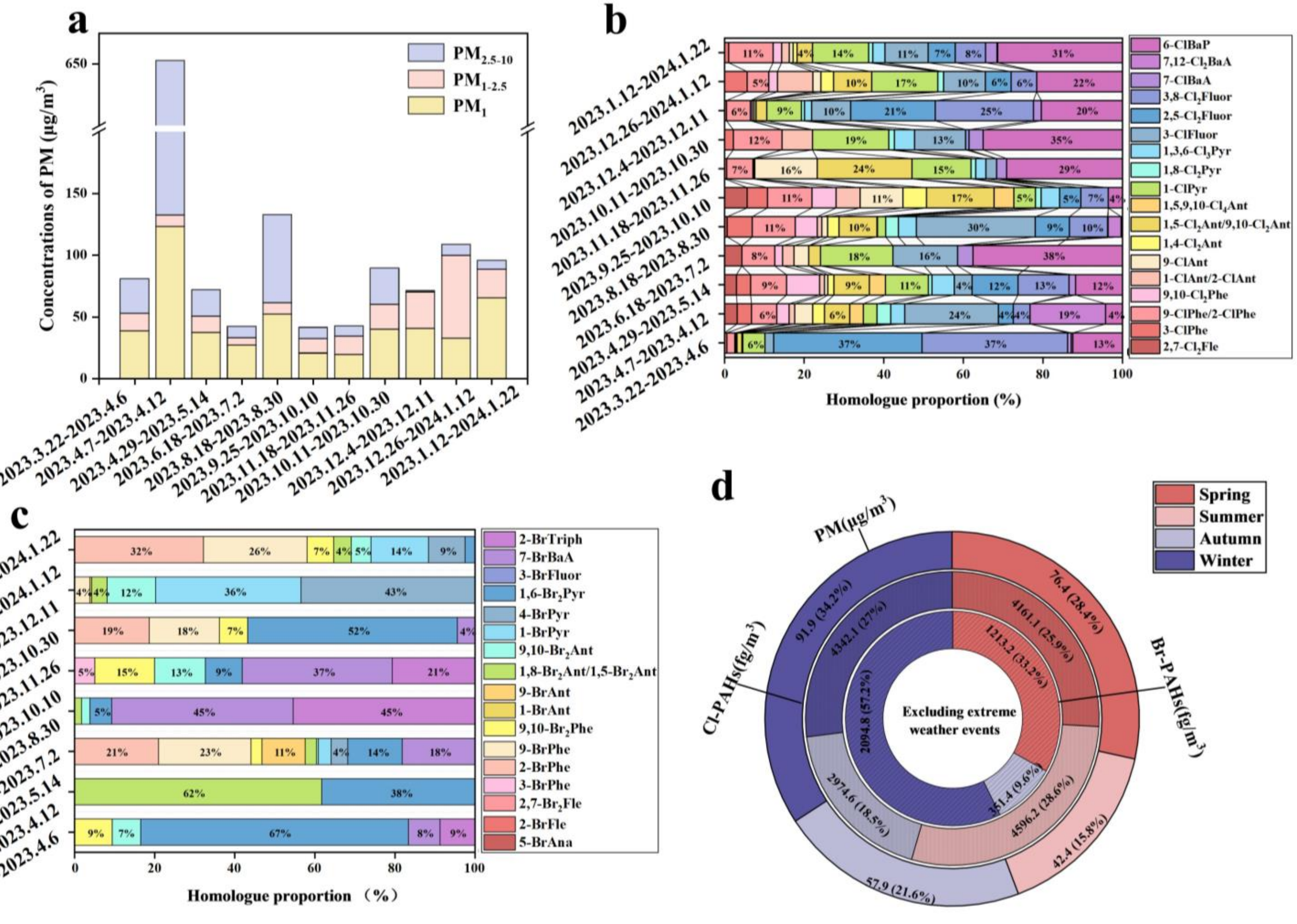


Fig. S2. (a) The distributions of PM with different diameters during the sampling period. (b-c) Stacked percentage graphs of individual ClPAHs and BrPAHs. (d) Seasonal distributions of PM, ClPAHs, and BrPAHs, excluding the extreme conditions.

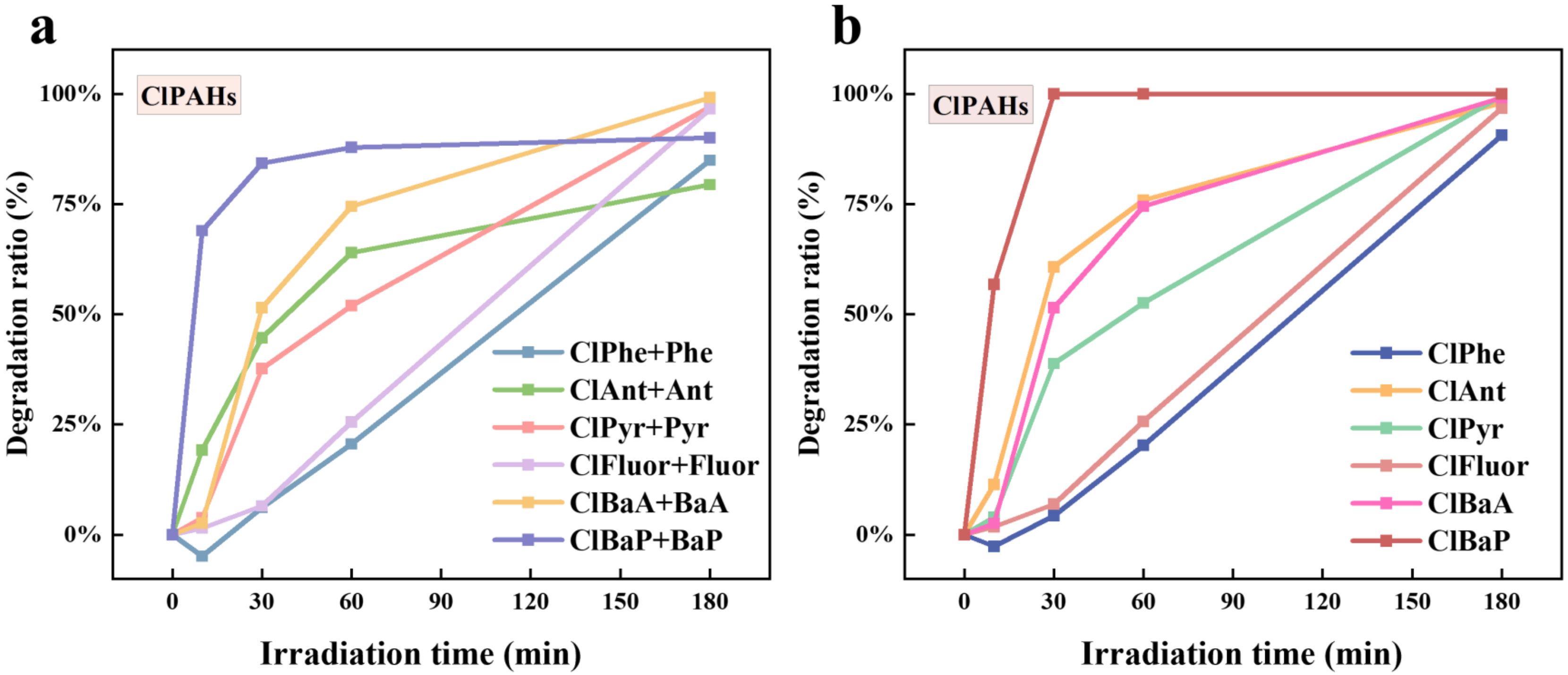


Fig. S3. Transformation ratios of (a) ClPAHs+PAHs and (b) ClPAHs under irradiation.

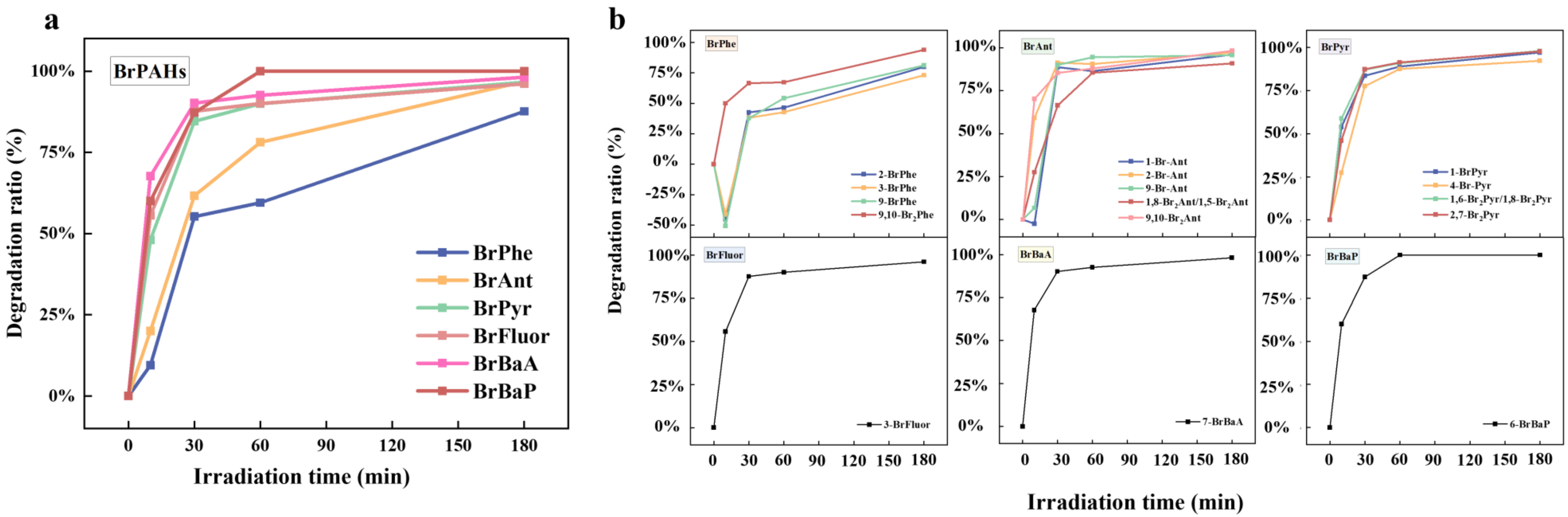


Fig. S4. Transformation ratios of (a) BrPAHs and (b) different monomers of BrPAHs under irradiation.

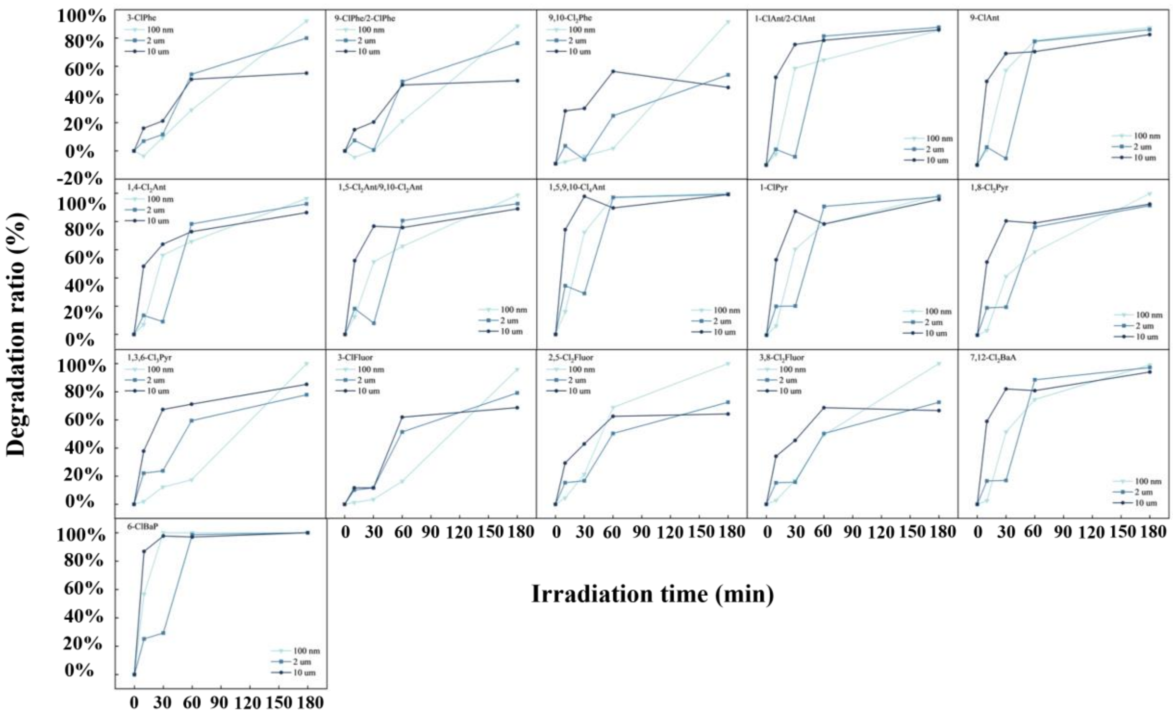


Fig. S5. The impact of particle size on transformation ratio of ClPAHs under irradiation.

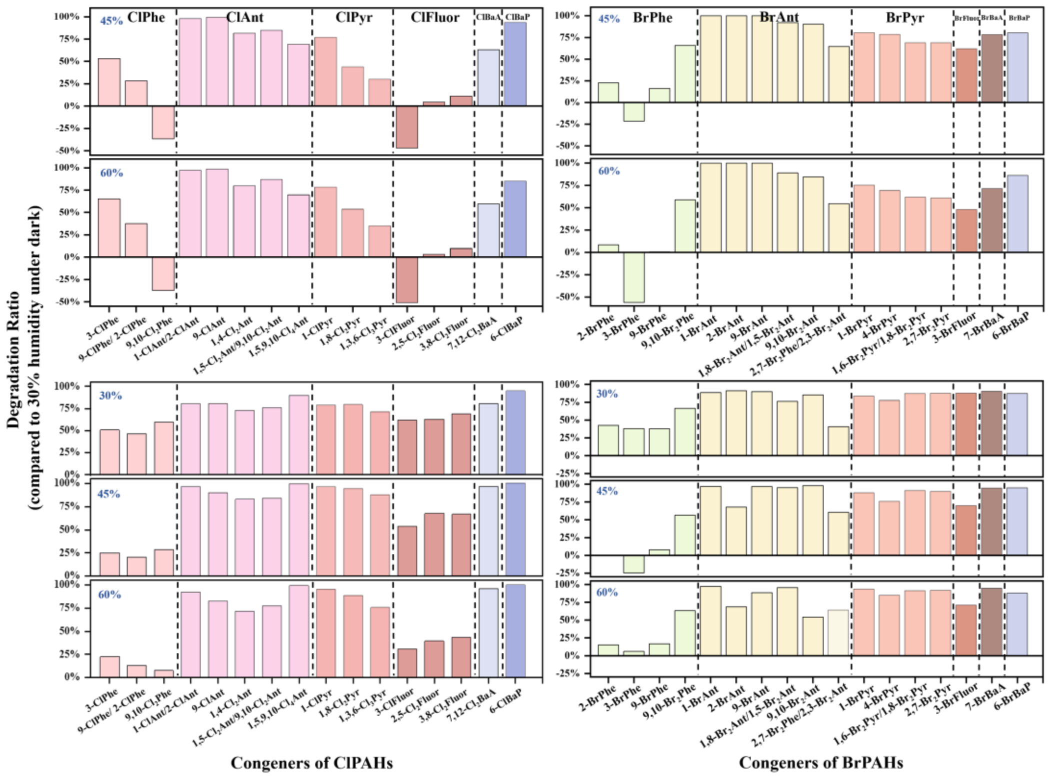


Fig. S6. Transformation ratios under different humidity conditions of (a) ClPAHs in the dark, (b) ClPAHs under irradiation, (c) BrPAHs in the dark and (d) BrPAHs under irradiation.

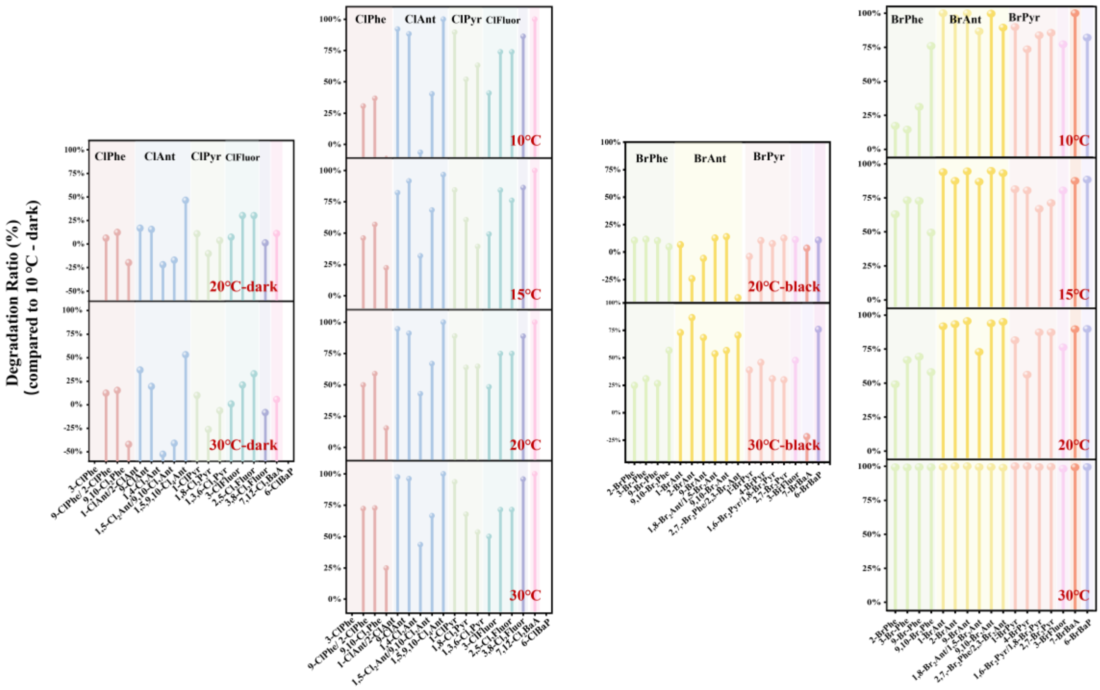


Fig. S7. Transformation ratios under different temperature conditions of (a) ClPAHs in the dark, (b) ClPAHs under irradiation, (c) BrPAHs in the dark and (d) BrPAHs under irradiation.

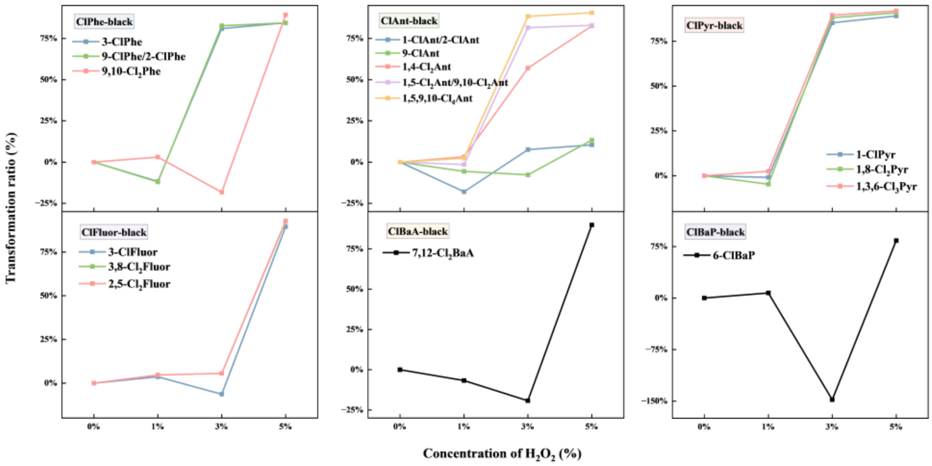
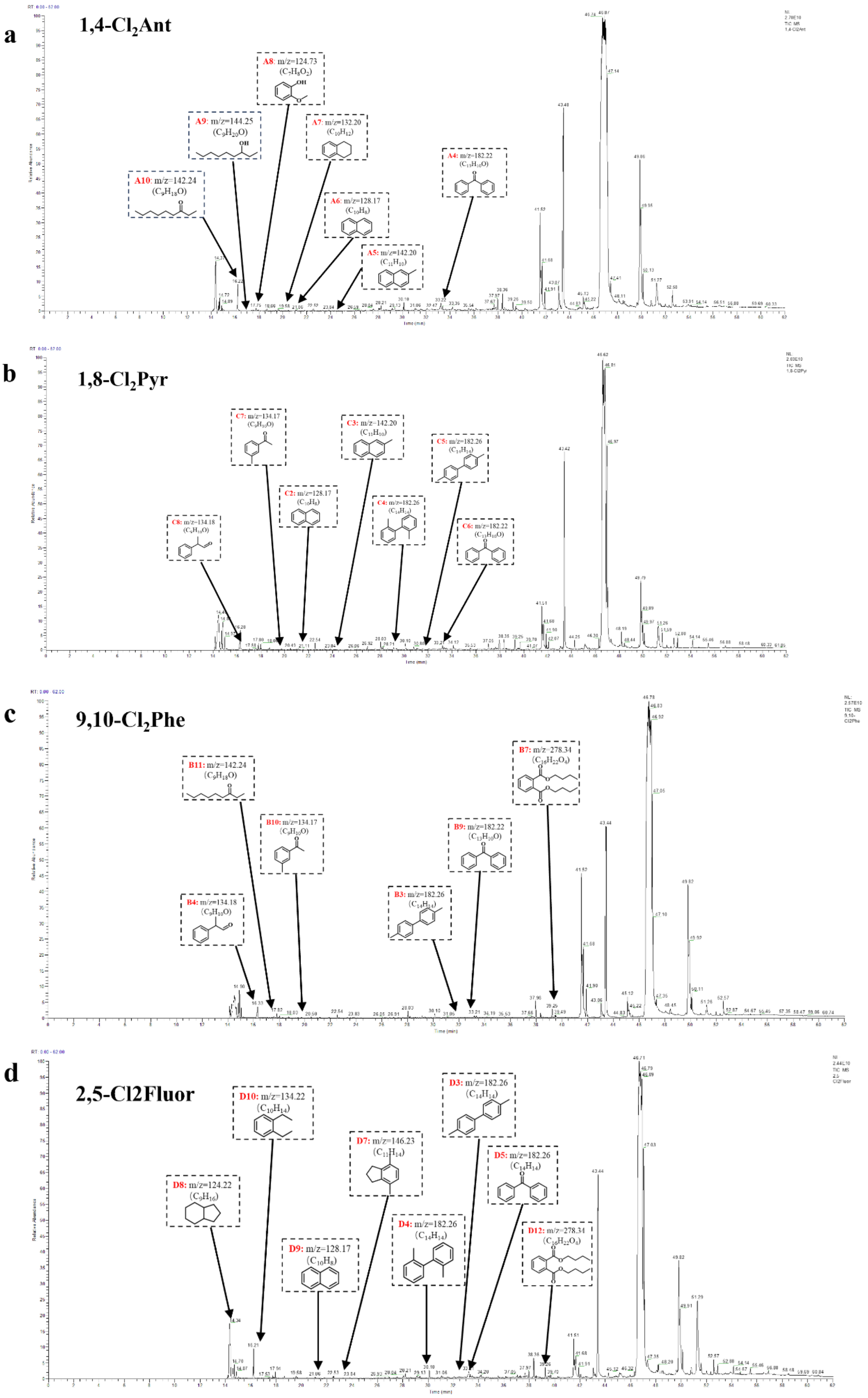
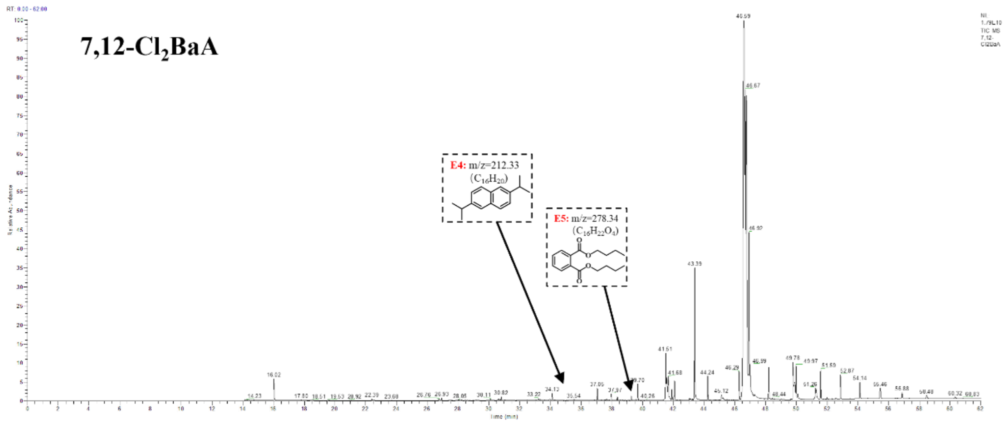


Fig. S8. Transformation ratios of ClPAHs under varying H_2O_2 concentrations in dark conditions.


a
1,4-Cl2Ant
A10: m/z=142.24 (C9H18O)
A9: m/z=144.25 (C9H20O)
A8: m/z=124.73 (C7H8O2)
A7: m/z=132.20 (C10H12)
A6: m/z=128.17 (C10H8)
A5: m/z=142.20 (C11H10)
A4: m/z=182.22 (C13H10O)
b
1,8-Cl2Pyr
C8: m/z=134.18 (C9H10O)
C7: m/z=134.17 (C9H10O)
C2: m/z=128.17 (C10H8)
C3: m/z=142.20 (C11H10)
C4: m/z=182.26 (C14H14)
C5: m/z=182.26 (C14H14)
C6: m/z=182.22 (C13H10O)
c
9,10-Cl2Phe
B11: m/z=142.24 (C9H18O)
B10: m/z=134.17 (C9H10O)
B4: m/z=134.18 (C9H10O)
B3: m/z=182.26 (C14H14)
B9: m/z=182.22 (C13H10O)
B7: m/z=278.34 (C16H22O4)
d
2,5-Cl2Fluor
D10: m/z=134.22 (C10H14)
D8: m/z=124.22 (C9H16)
D9: m/z=128.17 (C10H8)
D7: m/z=146.23 (C11H14)
D4: m/z=182.26 (C14H14)
D3: m/z=182.26 (C14H14)
D5: m/z=182.26 (C14H14)
D12: m/z=278.34 (C16H22O4)

e



f

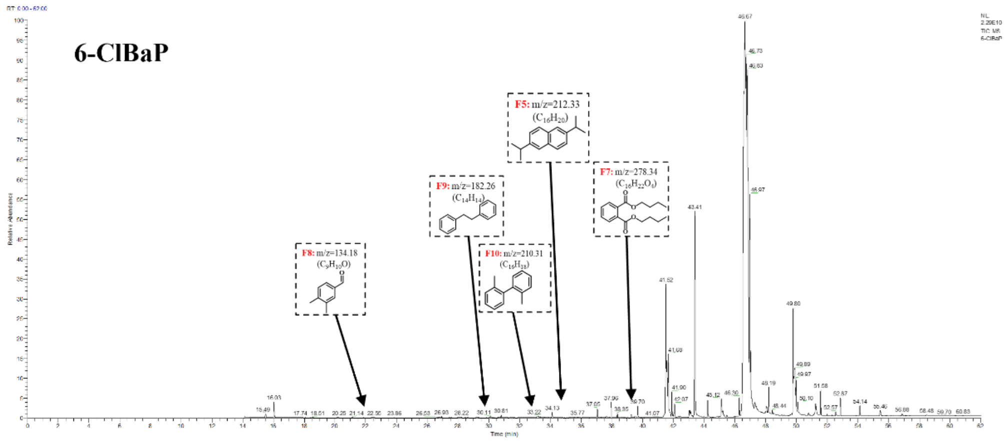


Fig. S9. Spectra of the transformation mechanisms of ClPAHs. (a) 1,4-Cl_2Ant. (b) 9,10-Cl_2Phe. (c) 1,8-Cl_2Pyr. (d) 2,5-Cl_2Fluor. (e) 7,12-Cl_2BaA. (f) 6-ClBaP.