Electronic Supplementary Material (ESI) for Analytical Methods.

Table S1

The experimental data for the peak areas of eight CPAHs obtained from Box–Behnken design DLLME conditions (n = 3).

Number	Factor			Peak Area								
	Extraction solvent volume	Disperser solvent volume	Extraction time	CPA	2,4-D	MCPA	2,4-DP	MCPP	2,4-DB	MCPB	Diclofop	Total
1	140	1	2	4.7	4.6	6.9	10.1	13.7	22.2	23.3	16.7	102.2
2	100	0.5	2	5.8	1.9	5	6.3	7.6	12	13.2	9.4	61.2
3	60	1	5	4.9	2.1	3	5.9	6.9	13.2	10.3	7.9	54.2
4	60	0.5	3.5	5	2.8	3.4	6.2	8.7	8.8	9.4	8.5	52.8
5	140	0.5	3.5	5.3	3.5	12.4	8.7	17	26	28	27	127.9
6	100	1	3.5	8.8	7.9	10	12	17.8	22.2	23.4	30.7	132.8
7	60	1	2	5	2.3	3	5.9	7.3	12.6	11.8	11.1	59
8	140	1	5	4.5	4.1	5.7	7.8	11	20	19	14	86.1
9	140	1.5	3.5	5.9	3	3.8	8.4	12	19.9	21	15.8	70.1
10	100	1	3.5	9	9.2	11	15.7	23	24	25.3	27.1	146.6
11	100	1	3.5	9.6	9.7	12.7	17.1	21.2	25.4	26	26	147.7
12	100	1	3.5	8.7	9.6	11.8	16.1	21.7	23.4	24.8	24.9	141
13	100	0.5	5	3	2.1	3.1	6.8	7.8	14	14	11.4	62.2
14	100	1	3.5	7.7	9.8	12.5	17	21.6	25.9	26.6	28.1	149.6
15	100	1.5	5	2.8	3	6.7	6.9	8.2	13.2	14.5	10	65.3
16	60	1.5	3.5	3	1.5	5.6	5.4	6	10.2	11.3	8.1	51.1
17	100	1.5	2	3.5	2.8	3	7.4	11.1	14	13.2	12.4	67.2

Table S2

The experimental data for the peak areas of eight CPAHs obtained from Box–Behnken design derivatization conditions (n = 3).

umber	Factor				Peak Area								
	T[1]	t[2]	C[3]	R[4]	CPA	2,4-D	MCPA	2,4-DP	MCPP	2,4-DB	MCPB	Diclofop	Total
1	100	15	12	6	25.4	24.9	33.2	26.3	65.6	67.9	99.1	41.6	384
2	85	10	20	10	11	11.3	15.5	12.8	33.2	40.4	56.4	21.6	202.2
3	100	5	12	6	11.5	11.7	15.6	12.4	31.8	38.7	55.8	20.7	160.2
4	85	5	12	2	1.9	1.9	2.7	2	7.8	9.2	13.1	9.8	48.4
5	85	15	20	6	9.2	9.6	13.3	11.7	30.2	35.5	49.9	19.3	178.7
6	85	10	12	6	33.5	31.2	45.4	35.7	60.4	88.3	120.6	56.8	471.9
7	70	15	12	6	3.2	3.3	5.1	3.8	10.9	15.8	22.3	17.7	82.1
8	85	10	12	6	31.2	29.8	36.2	33.7	63.9	71	105.5	47.9	419.2
9	70	10	12	10	6.2	6	8.5	5.8	17	28.4	39.8	12.2	123.9
10	85	10	4	10	17	16.5	22.1	17	44.2	57.3	79.6	29.4	283.1
11	70	10	20	6	3.4	3.4	4.8	3.4	9.9	16.1	22.9	18.6	82.5
12	85	5	20	6	4.6	4.8	6.7	4.9	13.9	19.9	28.2	9.7	92.7
13	85	10	12	6	29.1	27.9	34.7	31	58.2	83.2	99	44.1	397.1
14	85	15	12	10	17.6	17.6	23.7	19.1	48.9	58.2	81.2	31.9	298.2
15	70	10	4	6	4.1	3.9	5.3	3.5	10.2	16.9	23.2	15.5	50
16	85	10	20	2	2.2	2.3	3.3	2.5	7.2	9.5	13.6	8.8	49.4
17	85	10	12	6	31	29.6	42.3	37.6	62.1	76.1	106.7	39.6	425.1
18	100	10	12	2	8.5	8.4	12	10.6	25.4	30.9	45.7	16.8	158.3
19	85	10	4	2	3.9	3.7	5.1	3.5	10	17.1	24.4	19.2	86.9
20	85	15	12	2	3.3	3.4	4.7	3.5	9.9	14.3	20.4	6.9	66.4
21	100	10	4	6	25.9	33.8	34	36.7	47.9	64.3	90.6	42.8	376
22	100	10	20	6	18	16.5	26	24.4	50.5	61.7	87.1	37.3	320
23	85	15	4	6	15	14.5	19.6	14.9	39	52.6	75.1	26.2	257.9
24	85	5	12	10	9.2	9.3	12.8	9.1	25.4	37.2	52	17.9	172.9
25	85	10	12	6	25.4	26	33.2	38.6	61	72	95	54.3	405.5
26	70	5	12	6	2.4	2.3	3.3	2.5	10.4	12.1	17.1	17	67.1
27	70	10	12	2	1.3	1.2	1.8	1.4	6.8	6.5	9.1	3.9	32
28	85	5	4	6	7	6.7	9.2	6.3	17.8	28.4	39.6	24	139
29	100	10	12	10	27.5	32.3	35	27.3	52.8	71.1	101	42.3	389.3

[1] temperature (°C);[2] time (min); [3] amount of catalyst (mg); [4] molar ratio of BCETS to total CPAHs

Table S3

A comparison of the proposed method with different methods for detection of CPAHs.

Instrument method	Sample pretreatment	Sample pretreatment procedure/time/step	LOD	RSD%	Analytes	Samples	References
GC-MS	SBSE[1]	Adjusted the sample at pH 2, inserted the stir bars in sample, extracted for 240 min, rinsed stir bars with water, dried and inserted stir bars into a vial containing glass insert, desorbed the analytes for 30 min, removed the stir bar. > 7 steps, > 270 min.	20-46 ng/L	12-13	2,4-D, 2.4-DP, MCPB	Water	39
GC-MS	SPE[2]	Conditioned SPE cartridge: filtered cartridge, washed with ethyl acetate, methanol and water; adjusted sample pH, passed through a SPE cartridge, dried cartrige, eluted, added the mixture of PCB-30 in ethyl acetate, then evaporated. > 10 steps, > 50 min.	2-6 ng/mL	2.7-9	2,4-D, 2,4-DP, 2,4-DB, MCPA, MCPB	surface and sewage water	4
CE-UV	SPE-EME[3]	SPE: conditioned solid phase, loaded water sample, rinsed extraction column, adsorption, eluted, evaporated, redissolved and transferred to a vial; EME: conditioned hollow fiber (the end was closed), added acceptor phase, placed electrode, electro-extraction, cut the sealed end of the hollow fiber, collected acceptor phase. > 15 steps,	0.3-0.5 ng/mL	7-7.4	2,4-DP, MCPA, MCPP	Water	7
LC-UV	SPE	The SPE column was cleaned for 15 min and conditioned for 10 min, then sample were passed through the sorbent, performed two washing steps, then eluted and evaporated. > 7 steps	3.5-6 ng/mL	1-5	2,4-D, 2,4-DP, MCPA, MCPP, MCPB, 2,4,5-TP	Human urines samples	40
LC-MS/MS	LLE-SPE[4]	LLE: extracted with CH_2Cl_2, filtered through sodium sulfate, evaporated, reconstituted; SPE: Extraction cartridge was activated and washed, added reconstituted residues, washed the cartridges with NH_4OH and methanol, then eluted the target analytes. > 12 steps, > 30 min	0.4 ng/mL	-	2,4-D	Paddy field water	20
LC-MS-MS	SPE	Conditioned carbograph cartridge, fitted into filtering flask, liquids in a bottle connected to the sorbent cartridge were forced through the cartridge, washed cartridge with water, expelled remaining	1 ng/L	8	2,4-D, MCPA	River, draining and drinking water	41

		for 10 min and washed with methanol, eluted, evaporated and redissolved. > 10 steps					
LC-MS/MS	-	-	0.01-1.3 ng/mL	3-15	2,4-D, MCPA,MCPP, Haloxyfop, Fluazifop	Carrot, Apple	42
HPLC-UV	SPE	conditioned SPE cartridges with 3 steps, water samples were forced through the cartridge, then eluted with methanol and evaporated. > 6 steps	3-5 ng/mL	3	2,4-D, 2,4-DP, MCPA, MCPP	River water	43
HPLC-UV	HF-LPME[5]	Mounted the TT-extractor, pumped the organic solvent through the fiber channel, filled the fiber channel with organic solvent, pumped the aqueous sample around the fiber, washed the sample-phase channel with water and flushed the inside of the fiber with organic phase. > 35min, >6 steps	0.5 ng/mL	< 7	CPA	River water	44
HPLC-FLD	LLE	diluted samples with sodium chloride, added working solution, acidified the mixture and vortex, extracted with ethyl acetate/hexane, mixed vigorously for 5 min, centrifuged for 5 min, transferred the organic phase, evaporated > 25 min, > 9 steps	62.5 ng/mL	-	2,4-D, MCPA	Canine Plasma Urine	1
HPLC-FLD	Derivatization with 6-Oxy(acetylpiperazine) Fluorescein	Derivatization process was employed at 60 °C for 1 h in the dark.	4.43-14.2nM	1.05 -3.55	2,4-D	Cucumber, lettuce, tomato	45
HPLC-FLD	DLLME	Acidified the sample, rapidly injected a mixture of ACN and CH_2Cl_2, ultrasonic water bath, centrifuged, redissolved < 20 min, 5 steps	0.46-0.79 ng/mL	< 4.6	2,4-D, 2,4-DP, 2,4-DB, MCPA, MCPP, MCPB, CPA, Diclofop	Rice, Millet, Carrot, Pepper Tomato, Potato, Soybean,	This study

[1] Stir-bar Sorptive Extraction; [2] Solid-phase Extraction; [3] Solid Phase Extraction Combined with Electro Membrane Extraction; [4] Liquid–Liquid and Solid-phase Extraction; [5] Hollow Fiber Liquid-Phase Microextraction.

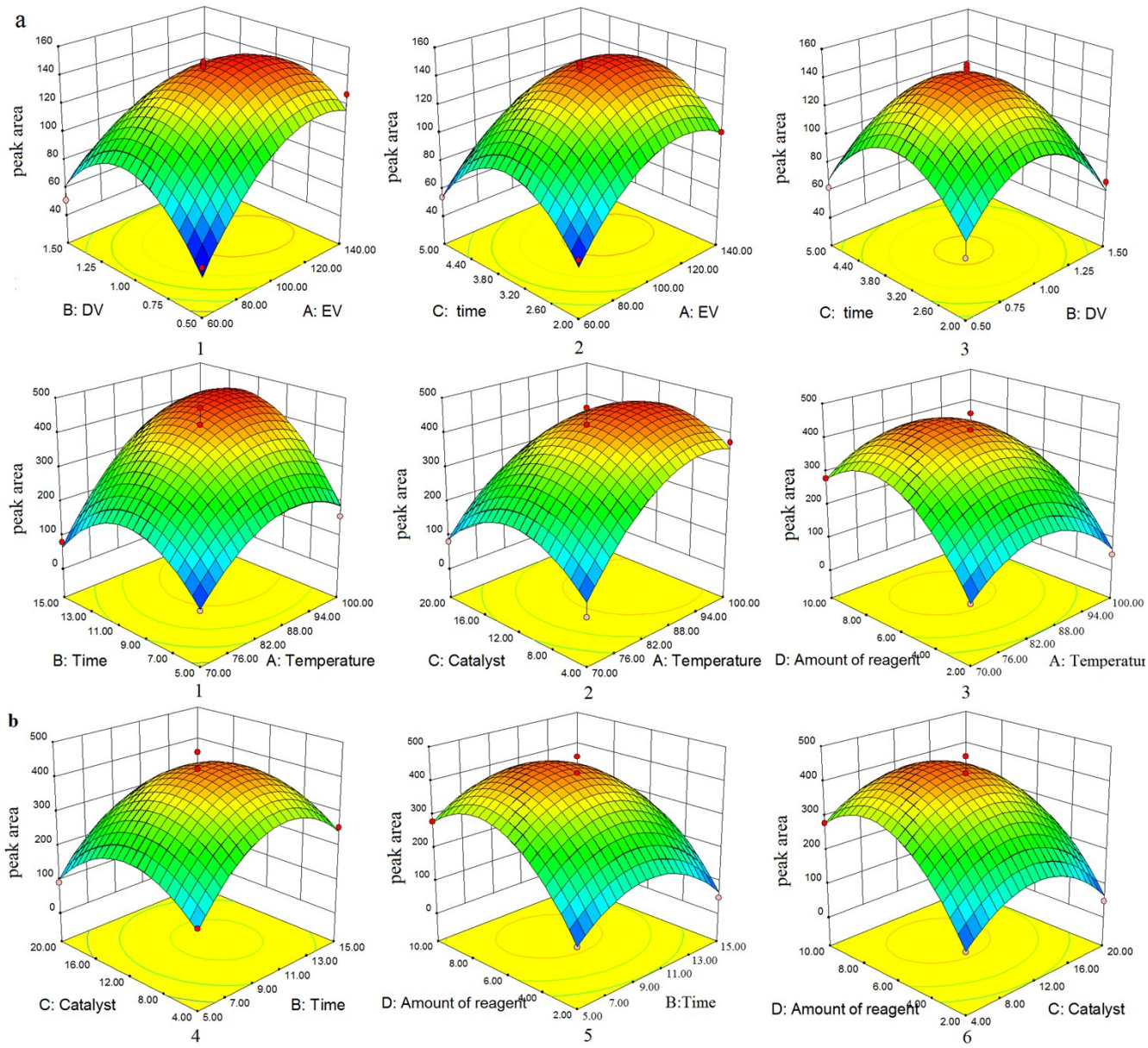

Figure S1. 3D surface for the interaction effects of the DLLME parameters a(1-3) and CPAHs derivatization b(1-6) using the BBD obtained by plotting. EV: extraction solvent volume; DV: disperser solvent volume.