Supporting Information

Identification of emerging brominated chemicals as the transformation products of tetrabromobisphenol A (TBBPA) derivatives in soil

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Instrumental Parameters of UHPLC-Orbitrap HRMS

Methanol (A) and water (B) were applied as mobile phases at a flow rate of 0.6 mL/min. The mobile phase gradient was initially 80:20 (v/v, A/B) and kept for 2 min, then increased to 100% A along 10 min and returned to 80:20 (v/v, A/B) in 1 min and then kept for 2 additional min. The recommended values were used in the full scan acquisition under heated electrospray ionization (HESI) mode without further optimization. The parameters used for the mass spectrometer were the following: full scan range (m/z), 100 to 1000; pray voltage, 2500 V; sweep gas flow rate, 1 respective arbitrary units; sheath gas flow rate, 40 respective arbitrary units; aux gas flow rate, 10 respective arbitrary units; ion transfer tube temperature, 350 °C; vaporizer temperature, 200 °C; MS^1 detector, Orbitrap; MS^1 resolution, 120,000; MS^1 scan range, 100-1000; MS^1 maximum injection time, 100 ms; MS^1 automated gain control (AGC) target, 100,000; S-lens RF level, 60 V; MS^2 higher-energy collisional dissociation (HCD) collision energy, 45%; MS^2 detector, Orbitrap; MS^2 isolation, 16; MS^2 resolution, 15,000; MS^2 AGC target, 50,000; MS^2 maximum injection time, 35 ms; MS^2 start mass, 50. Xcalibur Qual and Quan Browser software were used for the qualitative and quantitative calculation.

Elution Program Employed in HPLC-UV Analysis Thermo Utimate 3000 HPLC coupled with a UV detector were used for the instrumental analysis. And ZORBAX ODS (150 × 3.0 mm, 5 μm, Agilent) column was used for the purity analysis and degradation products analysis. Methanol (A) and water (B) were applied as the mobile phases at a flow rate of 0.35 mL/min. The flow gradient was 80:20 (v/v, A/B) initially, and kept for 2 min, then increased to 100% A in 9 min and held for 2 min. The gradient was then returned to 80:20 (v/v, A/B) in 1 min and kept for 2 min. The wavelength of UV detector was set at 214 nm.

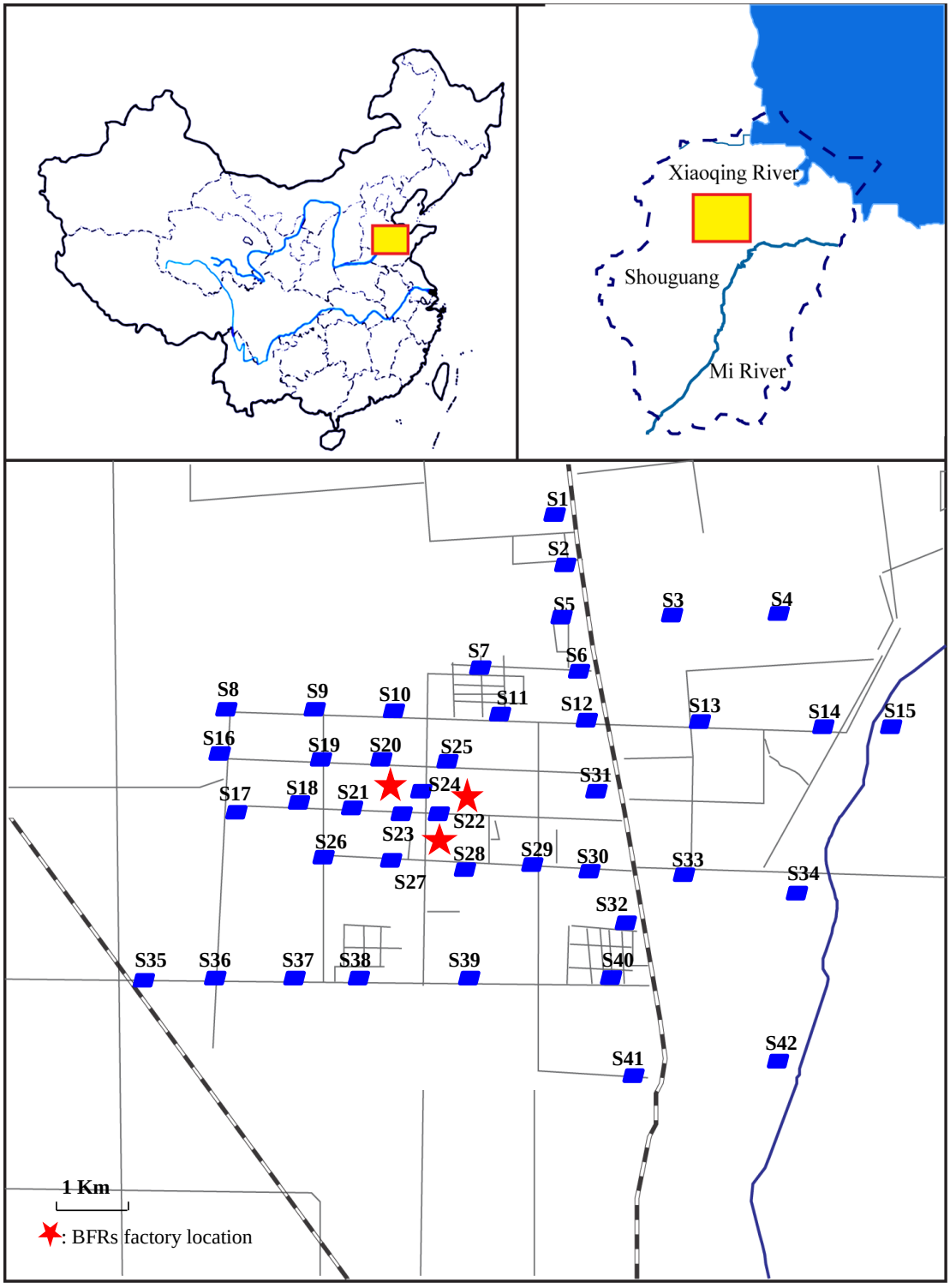


Figure S1. Sampling sites map.

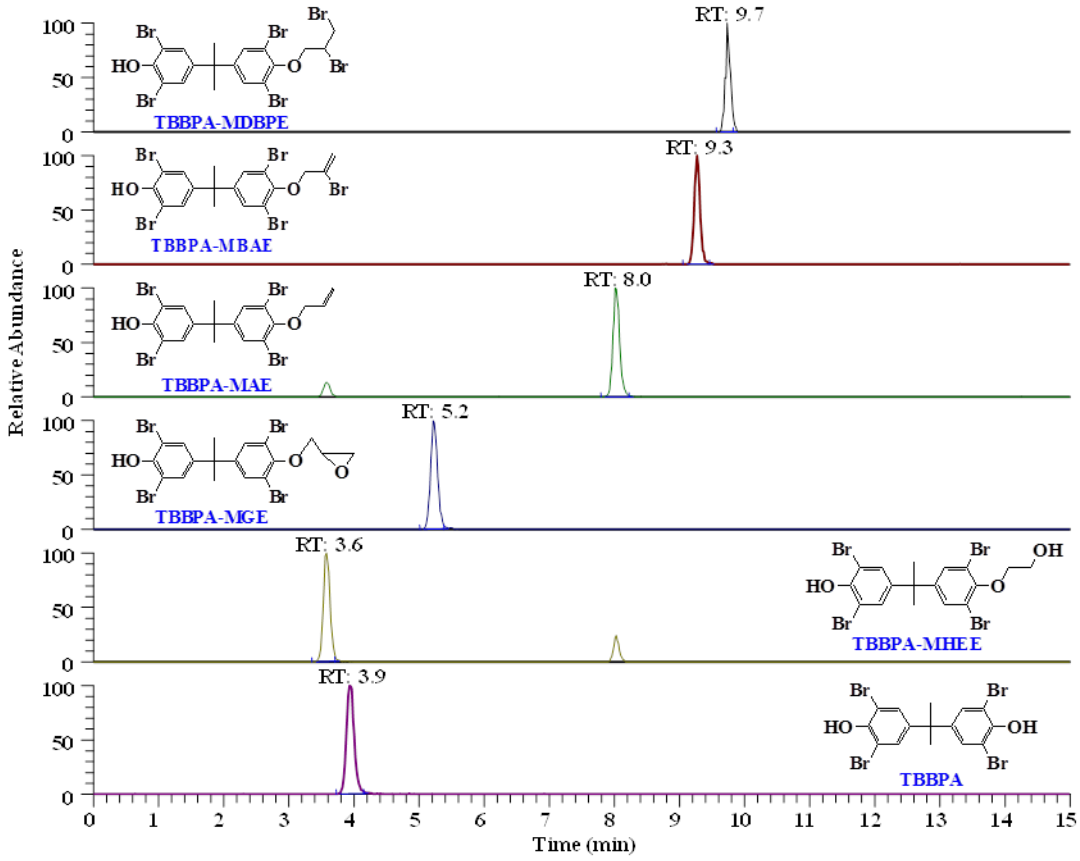


Figure S2. Mass chromatography of TBBPA and five TBBPA byproducts or possible transformation products.

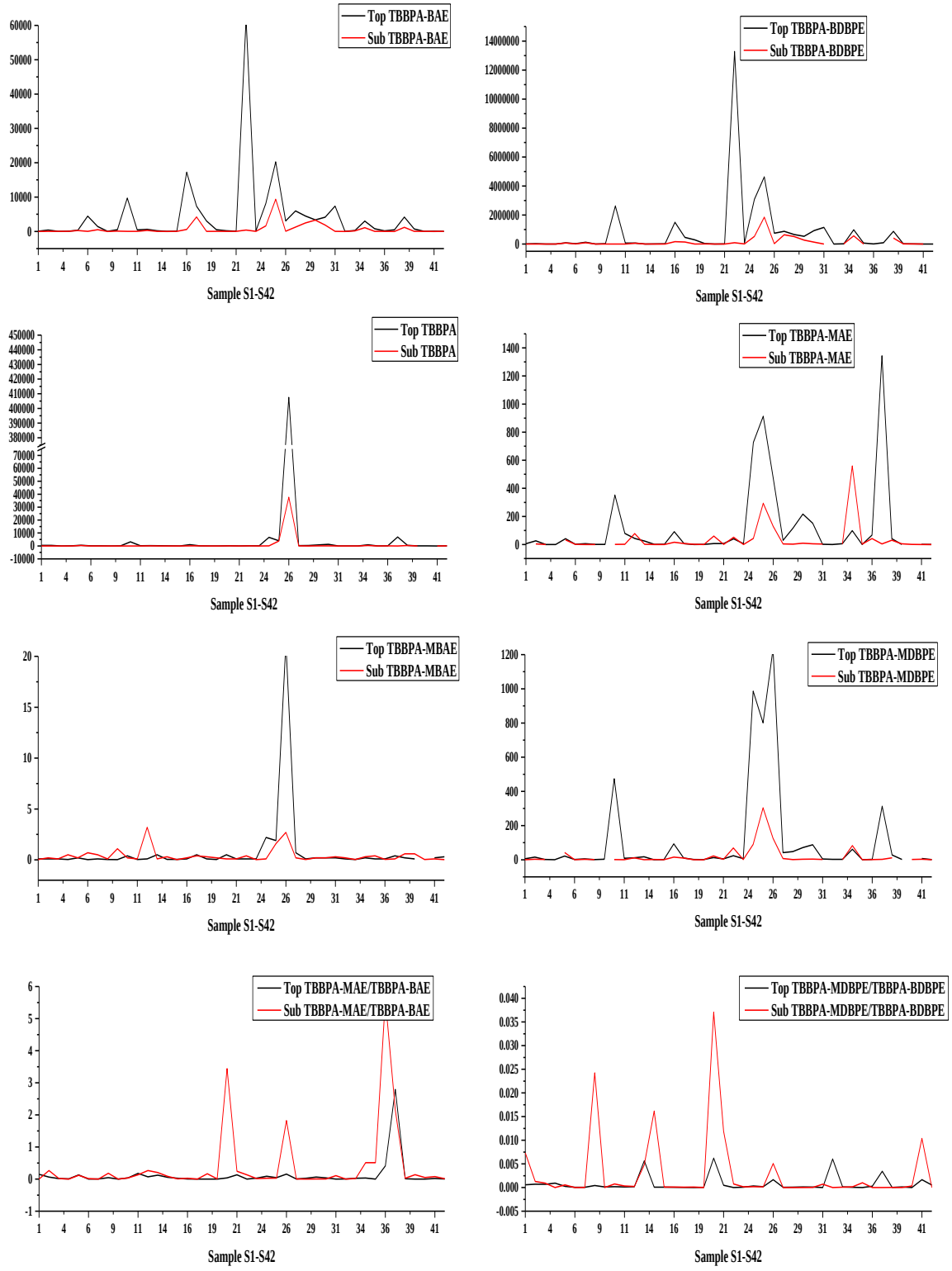


Figure S3. Concentration distribution in the top layer and sublayer soil samples for TBBPA, main derivatives and byproducts.

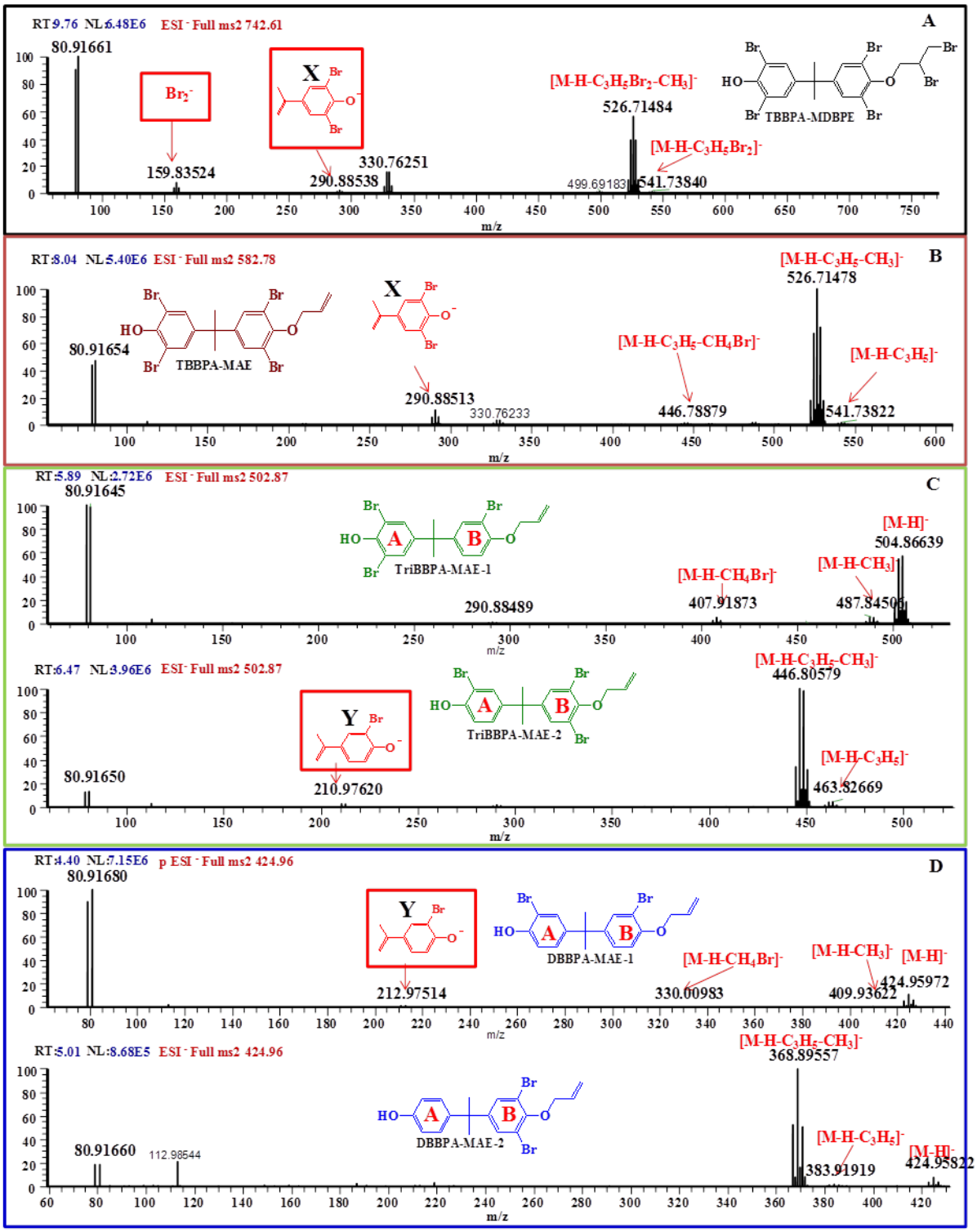


Figure S4. Mass spectrum of TBBPA-MDBPE, TBBPA-MAE and CCAs transformation products detected at RTs of 5.9/6.5, 4.4/5.0 min.

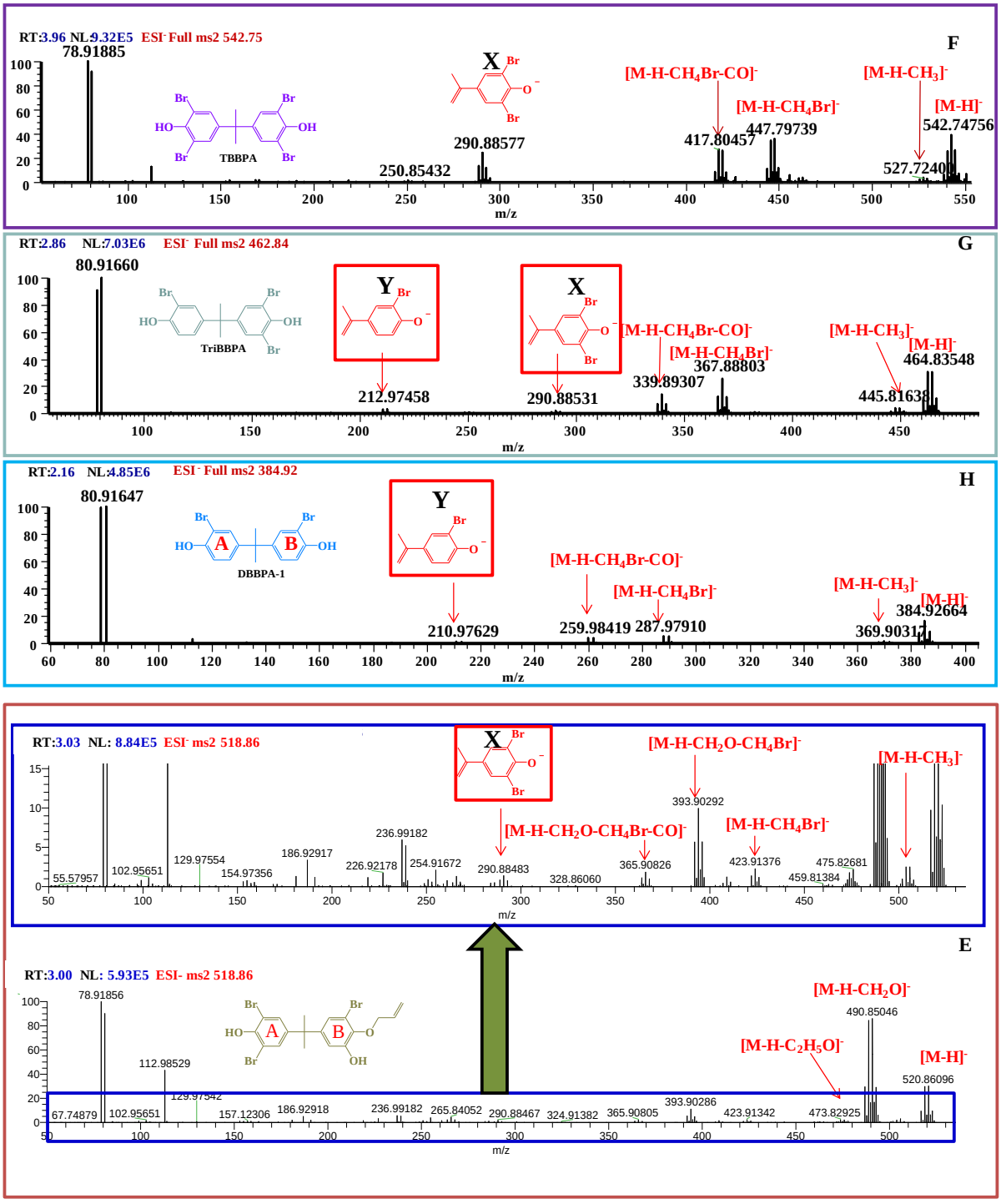


Figure S5. Mass spectrum of TBBPA and the CCAs transformation products detected at RTs of 2.9, 2.2 min and 3.0 min.

Structure Identification through the MS^2 Spectra of Figure S4 and S5. The same fragmentation steps of TriBBPA-MAE, TriBBPA-MAE (RT 6.5 min) and DBBPA-MAE (RT 5.0 min) for the precursor $[M-H]^-$ were observed by producing the segments $[M-H-C_3H_5]^-$ and $[M-H-C_3H_5-CH_3]^-$, which indicated the cleavage of ether bond and the loss of $\bullet CH_3$. TriBBPA-MAE (RT 6.5 min) and DBBPA-MAE (RT 5.0 min) probably had the similar structures with TBBPA-MAE, which indicated there are two bromine atoms at aromatic ring B. The two bromine atoms at aromatic ring B would be helpful for the cleavage of ether bond to form $[M-C_3H_5]^-$ in mass analysis. So the possible structures of TriBBPA-MAE (RT 6.5 min) and DBBPA-MAE (RT 5.0 min) would be TriBBPA-MAE-2 and DBBPA-MAE-2 in Figure S5, respectively. TriBBPA-MAE (RT 5.9 min) and DBBPA-MAE (RT 4.4 min), TriBBPA, DBBPA showed similar fragmentation behaviors with TBBPA by forming the segments $[M-H-CH_3]^-$ and $[M-H-CH_4Br]^-$. TBBPA has been reported to form 4-isopropylene-2,6-dibromophenol with a rearrangement of propyl group by the loss of dibromophenol moiety. [1, 2] The same fragments were also observed in the MS^2 spectra of TBBPA-MDBPE, TBBPA-MAE, TBBPA and TriBBPA (Figure S4 and S5, X). A 4-isopropylene-2,6-dibromophenol fragment was also observed in the MS^2 spectrum of HTriBBPA-MAE (Figure S5 E) which indicated there were two bromine atoms at aromatic ring A and the hydroxyl group might at ring B. The daughter ions at m/z 210.97620/212.97513 for TriBBPA-MAE, DBBPA-MAE, TriBBPA and DBBPA (Figure S4, S5, Y) might be 4-siopropyenr-2-bromophenol formed by the fragmentation at the same position with TBBPA-MDBPE, TBBPA-MAE, TBBPA and TriBBPA. Meanwhile, the daughter ion clusters at m/z 210.97705/212.97498 detected in DBBPA MS^2 spectrum (Figure S5 Y) indicated there was one bromine atom at ring A and B, respectively. The possible structures of the transformation products were shown in Figure S4 and S5. Further confirmation about the structures of the isomers is still relied on the commercial available standards of these compounds.

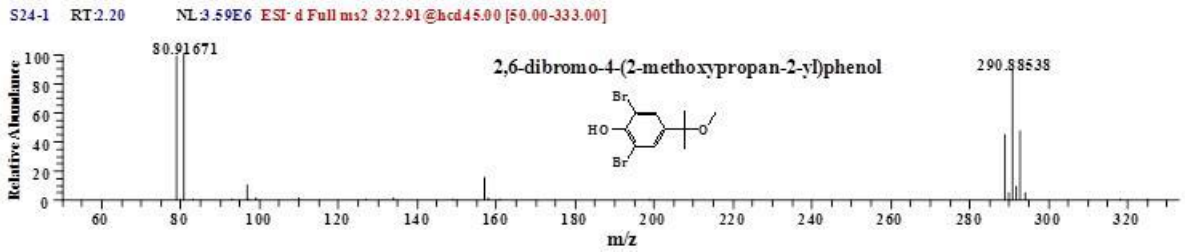


Figure S6. MS^2 spectrum of the non-targeted chemical NO.9.

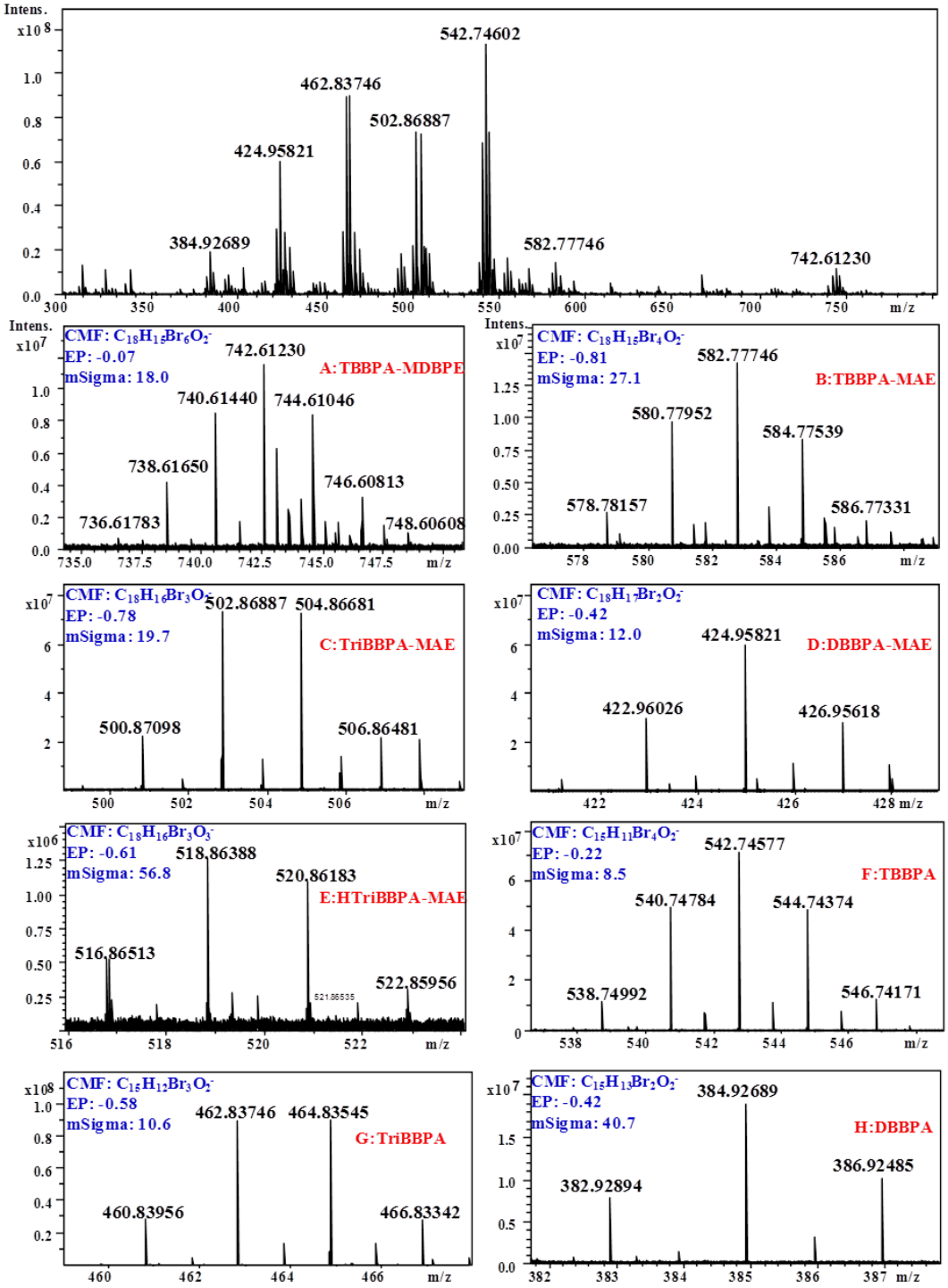


Figure S7. FTICR-MS spectra of the transformation products of TBBPA-MDBPE. CMF, calculated molecular formula given by Bruker Dltoncis SmartFormula with a mass deviation tolerance of 1 ppm; **EP**, error ppm, the value expresses the deviation with the theoretical molecular formula; **mSigma**, the isotope pattern matching factor, indicates the agreement between the measured and the theoretical isotopic pattern of the target compounds.

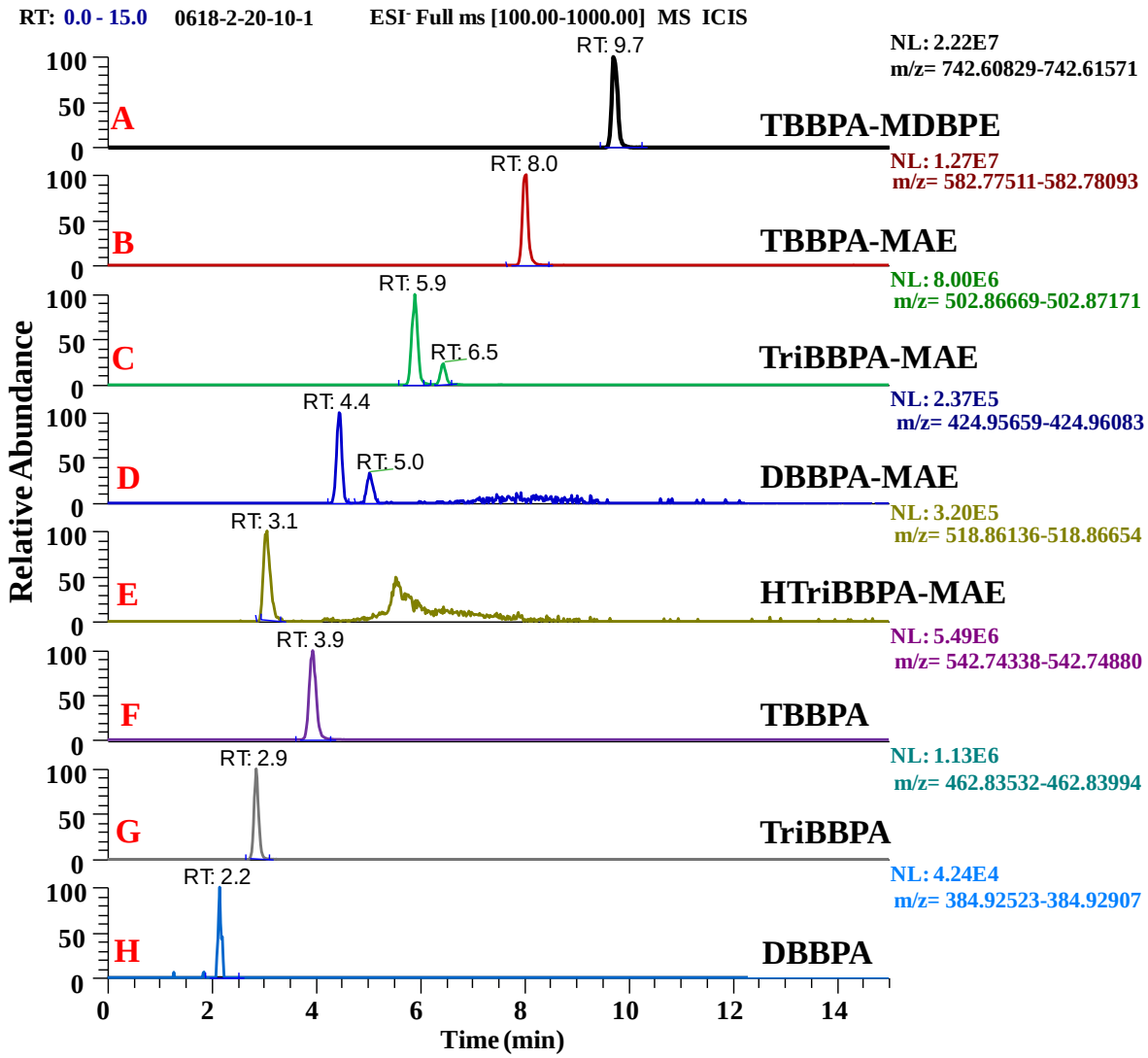


Figure S8. Mass chromatography of transformation products of TBBPA-MDBPE.

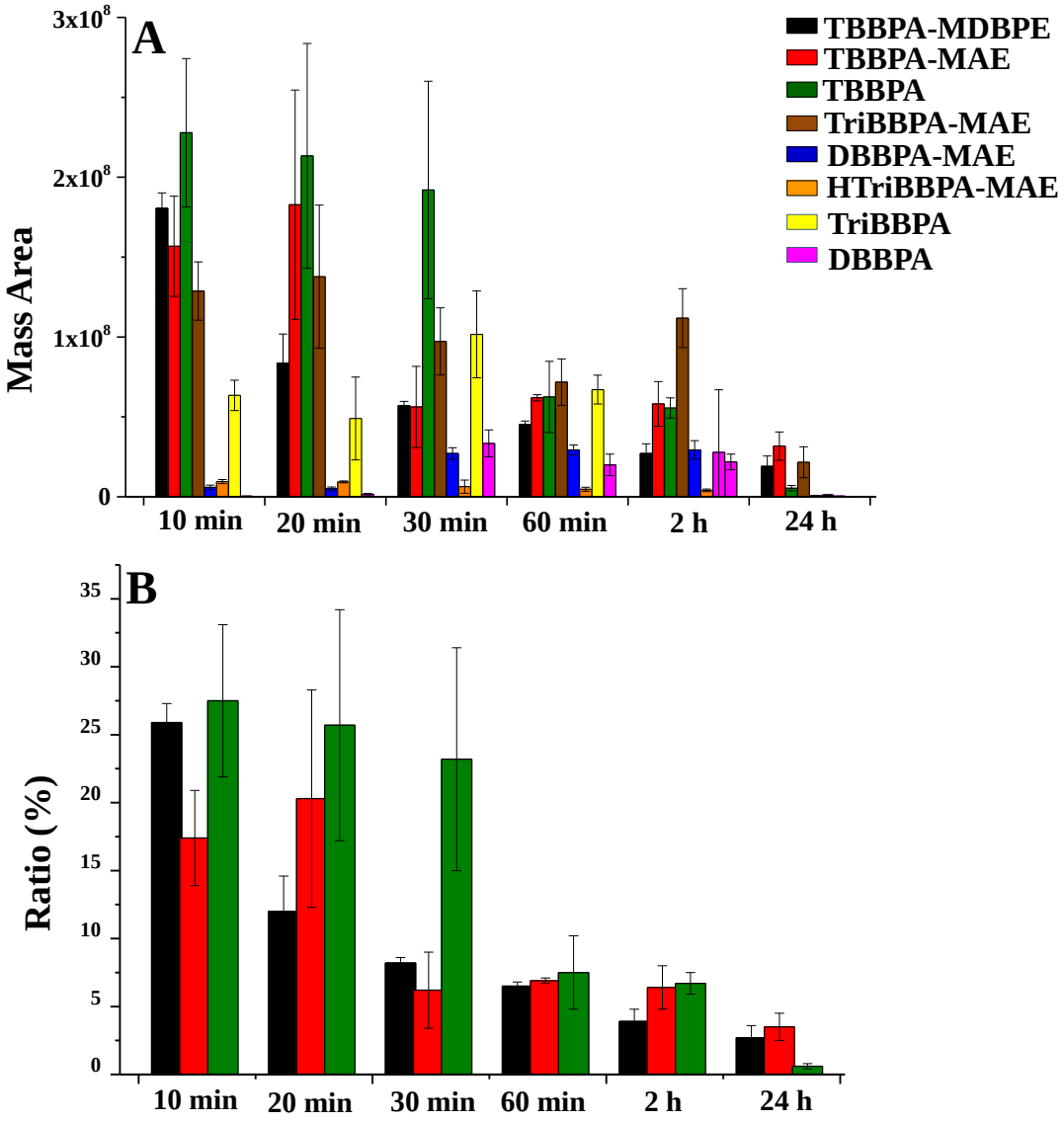


Figure S9. Transformation of TBBPA-MDBPE in 24 hours. (A) based on the mass area of the analytes. (B) based on the molar ratio of the analytes compared to the initial TBBPA-MDBPE.

Synthesis Procedure and ^{1}HNMR Data.

TBBPA-MDHPE

To a solution of TBBPA-MAE (584 mg) in acetone (2 mL) and water (5 mL), NMO (N-methyl morpholine-n-oxide) and OsO_4 was added at room temperature under the protection of N_2 flow. After the reaction mixture was stirred under ice bate condition for 2 hours, then at room temperature for 12 hours. After the reaction was completed, the reaction mixture was added 200 mg sodium dithionite, 2 g magnesium silicate and diluted with 8 mL water. After being shaked for 30 minutes the residue was removed. Tthe solution was adjusted to pH=2 with H_2SO_4, and extracted with DCM and purified with gel chromatography, giving TBBPA-MDHPE in a yield of 87%.

^{1}HNMR (400 MHz, DMSO) δ 9.858 (s, 1 H), 7.439 (s, 2 H), 7.368 (s, 2 H), 4.960 (s, 1H) 4.619 (s, 1 H), 3.861-3.899 (t, 3 H), 3.426-3.538 (m, 1 H), 3.341-3.415 (d, *J*=29.6 Hz, 1 H), 1.586 (s, 6 H); UHPLC-Orbitrap-HRMS (ESI) caled for $C_{18}H_{17}Br_4O_4^-$ [M - H]$^-$ 616.78249, found 616.78241.

TBBPA-MBHPE

To a solution of TBBPA-MGE (600 mg) in $CHCl_3$ (30 mL), 82 μL HBr (47% in water) was added dropwise. After being stirred at room temperature for 8 hours, the reaction mixture was diluted with 50 mL water and extracted with DCM. After concentrated with rotary evaporator, the residue was purified with gel chromatography, giving TBBPA-MBHPE in a yield of 85%.

^{1}HNMR (400 MHz, DMSO) δ 9.844 (s, 1 H), 7.455 (s, 2 H), 7.371 (s, 2 H), 5.602-5.616 (d, *J*= 5.6 Hz, 1H), 4.060-4.113 (m, 1 H), 3.932-3.946 (d, *J* = 5.6 Hz, 2 H), 3.719-3.755 (m, 1 H), 3.577-3.617 (m, 1 H), 1.589 (s, 6 H); UHPLC-Orbitrap-HRMS (ESI) caled for $C_{18}H_{16}Br_5O_3^-$ [M - H]$^-$ 678.69809/680.69604, found 678.69812/680.69598.

TBBPA-MHPE

To a solution of TBBPA-MAE (584 mg) in anhydrous THF (20 mL), 9-BBN (9-Borabicyclo [3.3.1] nonane, 610 mg) was added at room temperature. After the reaction

mixture was stirred under a mild N_2 flow for 12 hours, 3 mL Sodium hydroxide solution (360 mg in 3 mL water) was added at one time, then, 3 mL H_2O_2 (30%) was added dropwise in 10 to 15 minutes. The reaction mixture was then stirred at room temperature for 5 hours. After the reaction was completed, the reaction mixture was diluted with CH_2Cl_2 and washed with saturated solution of sodium bicarbonate and water. The organic layer was dried over anhydrous $MgSO_4$. After removal of the organic solvent, the residue was purified by column chromatography, giving TBBPA-MHPE in a yield of 60%.

^{1}HNMR (400 MHz, DMSO) δ 7.437 (s, 2 H), 7.364 (s, 2 H), 4.016-3.983 (t, J = 13.2, 6.8 Hz, 2 H), 3.624-3.593 (t, J = 12.4, 6.4 Hz, 2 H), 2.083 (s, 2 H), 1.960-1.896 (m, 2 H), 1.585 (s, 6 H); UHPLC-Orbitrap-HRMS (ESI) caled for $C_{18}H_{17}Br_4O_3^-$ $[M - H]^-$ 600.78757, found 600.78748.

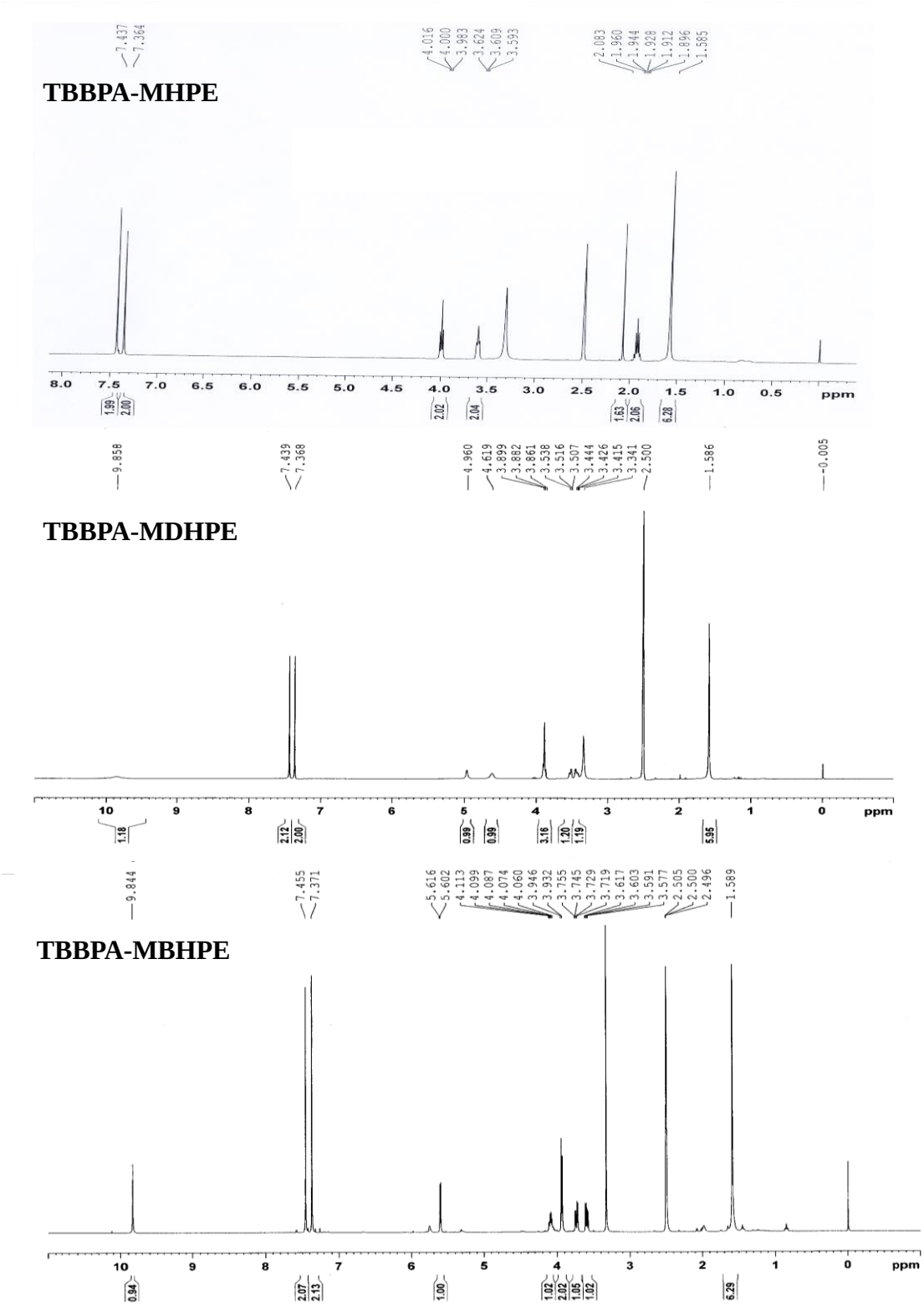


Figure S10. [1]HNMR spectrum of synthesized TBBPA-MHPE, RBBPA-MDHPE and TBBPA-MBHPE.

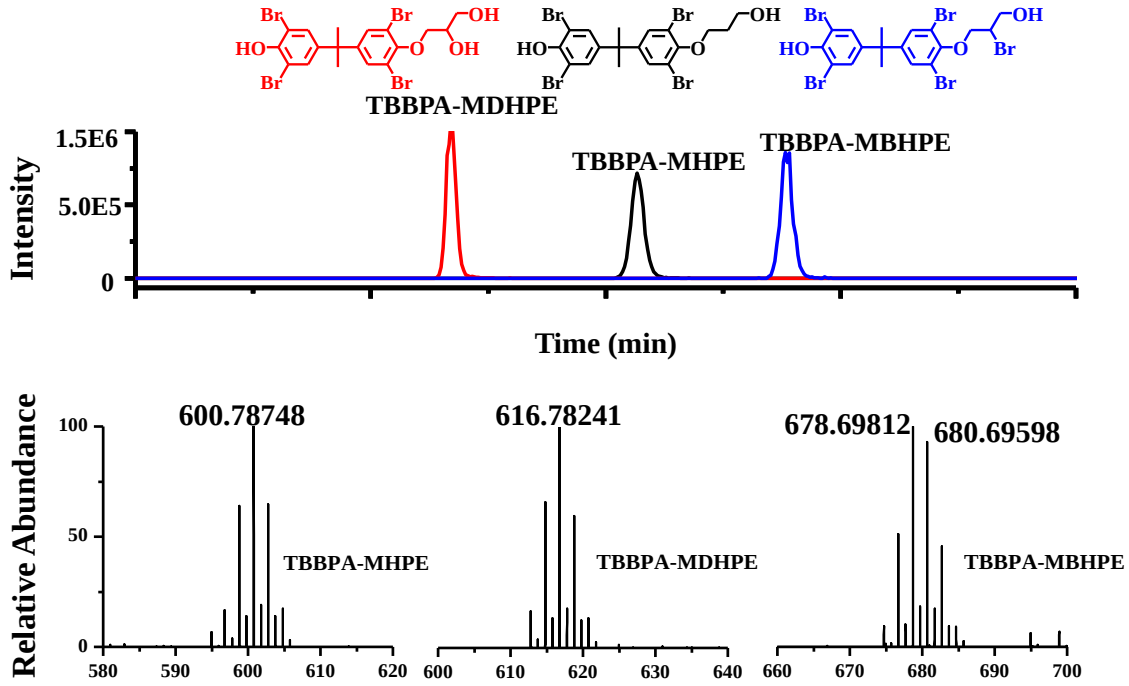
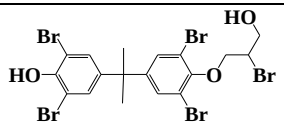
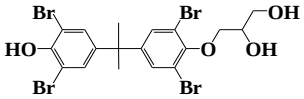
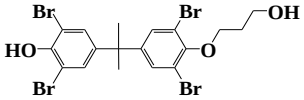
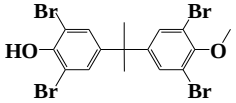
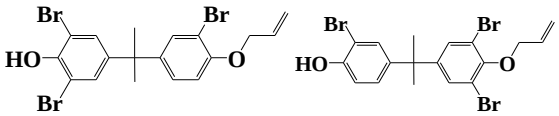
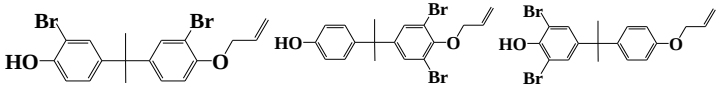
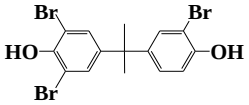
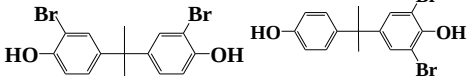
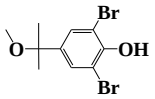
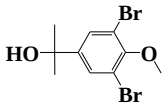
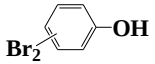
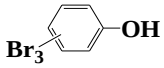
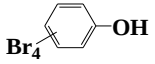
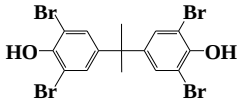
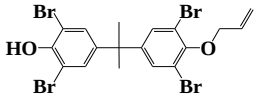
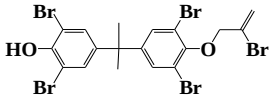


Figure S11. HRMS chromatography and spectra of synthesized TBBPA-MDHPE, TBBPA-MBHPE and TBBPA-MHPE.

Table S1. Chemicals and their structures detected in transformation process and soil samples.

Chemicals NO.	Abbreviation	Full name	Structure [a] or possible structure [b]	
1	TBBPA-MBHPE	TBBPA mono(2-bromo-3-hydroxypropyl ether)		*a*
2	TBBPA-MDHPE	TBBPA mono(2,3-dihydroxypropyl ether)		*a*
3	TBBPA-MHPE	TBBPA mono(3-hydroxypropyl ether)		*a*
4	TBBPA-MME	TBBPA mono(methyl ether)		*a*
5	TriBBPA-MAE	TriBBPA mono (allyl ether)		*b*
6	DBBPA-MAE	DBBPA mono (allyl ether)		*b*
7	TriBBPA	tribromobisphenol A		*a*
8	DBBPA	dibromobisphenol A		*b*

Continued

Chemicals NO.	Abbreviation	Full name	Structure [a] or possible structure [b]	
9		2,6-dibromo-4-(2-methoxypropan-2-yl)phenol		[b]
		2,6-dibromo-4-(2-(2-hydroxy)-propyl)-methoxybenzene		[b]
10	DBP	dibromophenol		[b]
11	TriBP	tribromophenol		[b]
12	TeBP	tetrabromophenol		[b]
13	MHDBDE	methoxyl-hydroxy-dibromobispenylether		
14	HPBDE	hydroxy-pentabromodiphenylether		
15	TBBPA	tetrabromobisphenol A		[a]
16	TBBPA-MAE	TBBPA mono(allyl ether)		[a]
17	TBBPA-MBAE	TBBPA mono(2-bromoallyl ether)		[a]

Continued

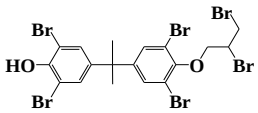
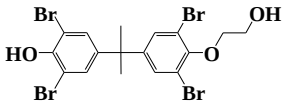
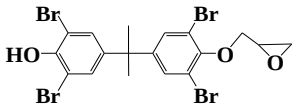
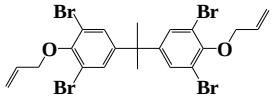
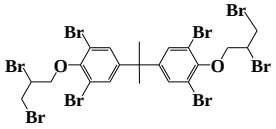
Chemicals NO.	Abbreviation	Full name	Structure [a] or possible structure [b]	
18	TBBPA-MDBPE	TBBPA mono(2,3-dibromopropyl ether)		*a*
19	TBBPA-MHEE	TBBPA mono(2-hydroxyethyl ether)		*a*
20	TBBPA-MGE	TBBPA mono(glycidyl ether)		*a*
21	TBBPA-BAE	TBBPA bis(allyl ether)		*a*
22	TBBPA-BDBPE	TBBPA bis(2,3-dibromopropyl ether)		*a*

Table S2. Instrumental parameters of FT-ICR MS.

API Source and Mode			
API Source		*Mode*	
Source Type	ESI (-)	Detection mode	Broadband
Capillay +	4000 V	TD(acquisition)	4M
End Plate Offset	—500 V	TD(Tune/Display)	4M (Full Resolution)
Dry Gas	2.0 L/min	Estimate R.P	240000 at m/z 400
Dry Tem	180 ºC	Transient Length	0.8389 sec
Ion Transfer			
Source Optics		*Collision Cell*	
Capillary Exit	—200.0 V	Collision Voltage	4.0 V
Deflector Plate	—180.0 V	DC Extract Bias	(-0.5) V
Funnel 1	—100 V	RF frequency	2 MHz
Skimmer 1	—25.0 V	Collision RF Amplitude	600.0 vpp
Funnel RF Amplitude	130.0 vpp		
Octopole		*Transfer Optics*	
Trequency	5 MHz	Time of Flight	0.6 ms
RF Amplitude	200.0 vpp	Frequency	2 MHz
Quadrupole		RF Amplitude	150.0 vpp
Q1 Mass	100.0 m/z		

Table S3. Method performance data for the analytical method.

		TBBPA	TBBPA -BAE	TBBPA-BDBPE	TBBPA -MAE	TBBPA -MBAE	TBBPA-MDBPE	TBBPA-MGE	TBBPA-MHEE	TBBPA -MHPE	TBBPA -MDHPE	TBBPA -MBHPE
Soil	Recovery	85%	94%	95%	78%	86%	92%	86%	88%	92%	94%	95%
	MDL(ng/g dw)	0.1	0.4	3	0.02	0.02	0.09	0.08	0.09	0.06	0.12	0.06

Table S4. Targeted concentrations (ng/g dw) of TBBPA analogs in soil samples. [a]

	TBBPA-BAE	TBBPA-BDBPE	TBBPA	TBBPA-MAE	TBBPA-MBAE	TBBPA-MDBPE	TBBPA-MHEE	TBBPA-MDHPE	TBBPA-MHPE	TBBPA-MGE	TBBPA-MBHPE	TOC	PH
S1-1	40.0	9862.2	444.9	6.0	0.1	5.8	ND	ND	ND	ND	0.2	0.67%	8.15
S1-2	2.0	41.0	3.7	ND	0.04	0.3	ND	ND	ND	ND	ND	0.24%	8.40
S2-1	413.3	21704.1	448.2	26.1	0.1	15.4	ND	ND	ND	0.2	1.2	0.97%	8.02
S2-2	16.8	2579.5	18.2	4.5	0.2	3.3	ND	ND	ND	ND	ND	0.52%	8.08
S3-1	20.3	2946.3	14.9	0.3	0.1	2.0	ND	ND	ND	ND	ND	0.52%	9.35
S3-2	11.7	1842.5	9.8	0.2	0.1	1.7	ND	ND	ND	ND	ND	0.47%	8.80
S4-1	53.8	530.2	39.8	0.3	0.04	0.5	ND	ND	ND	ND	ND	0.26%	8.24
S4-2	4.1	195.7	2.4	ND	0.5	ND	ND	ND	ND	ND	ND	0.36%	8.15
S5-1	317.3	82256.9	486.4	41.2	0.2	21.6	0.05	ND	1.0	0.5	0.8	1.17%	8.33
S5-2	273.2	77542.9	309.0	32.6	0.2	42.7	ND	ND	1.7	ND	0.2	1.14%	8.06
S6-1	4464.5	27270.7	69.8	1.2	0.03	1.6	ND	ND	ND	ND	0.2	0.31%	8.54
S6-2	33.0	7209.6	19.7	0.5	0.7	0.1	ND	ND	ND	ND	ND	0.46%	8.64
S7-1	1441.3	123625.6	109.6	5.4	0.1	5.5	ND	ND	0.04	ND	ND	0.18%	8.49
S7-2	505.3	90310.8	15.2	0.3	0.5	2.5	ND	ND	ND	ND	ND	1.24%	7.39
S8-1	17.6	2560.1	19.8	0.8	0.04	1.1	ND	ND	ND	ND	0.2	0.72%	8.29
S8-2	1.1	37.1	1.4	0.2	0.1	0.9	ND	ND	ND	ND	ND	0.80%	8.46
S9-1	512.0	21621.0	22.6	0.7	0.03	2.9	ND	ND	ND	ND	ND	0.28%	8.39
S9-2	85.0	2506.8	2.9	ND	1.1	ND	ND	ND	ND	ND	ND	0.49%	7.70
S10-1	9703.3	2624049.6	3214.9	351.8	0.4	474.2	3.7	0.5	3.3	4.6	12.5	1.41%	7.46
S10-2	14.2	1441.4	10.1	0.5	0.2	1.1	ND	ND	ND	ND	ND	0.36%	8.32
S11-1	441.2	68755.9	187.8	78.7	0.04	8.5	ND	ND	0.1	1.1	1.6	0.54%	8.18
S11-2	12.8	2109.4	6.6	1.7	0.1	0.7	ND	ND	ND	ND	ND	0.28%	9.46
S12-1	620.4	67960.9	223.9	42.9	0.1	11.3	ND	ND	ND	0.7	2.0	0.06%	8.31
S12-2	291.6	53879.0	58.3	77.4	3.2	11.6	ND	ND	ND	4.3	3.4	0.85%	7.96
S13-1	195.5	3055.5	143.0	24.2	0.5	17.3	ND	ND	ND	1.1	1.5	0.67%	8.40
S13-2	6.9	146.1	15.9	1.4	0.1	0.7	ND	ND	ND	ND	ND	0.38%	8.13
S14-1	15.8	5987.7	43.1	0.9	0.05	0.5	ND	ND	ND	ND	ND	0.46%	8.05
S14-2	3.5	111.3	3.0	0.3	0.3	1.8	ND	ND	ND	ND	ND	0.83%	7.94
S15-1	60.0	13520.0	18.3	1.6	0.05	1.1	ND	ND	ND	ND	ND	0.61%	8.32
S15-2	15.9	2850.3	0.1	0.1	0.03	0.3	ND	ND	ND	ND	ND	0.35%	8.48
S16-1	17244.1	1504072.6	944.9	91.4	0.1	93.1	0.1	0.2	0.1	1.0	3.5	0.66%	8.75
S16-2	571.4	164960.2	59.4	15.8	0.2	15.3	ND	ND	ND	ND	0.4	0.85%	8.40
S17-1	7361.5	461392.0	35.0	5.8	0.5	10.0	ND	ND	ND	ND	ND	0.90%	8.65
S17-2	4203.8	136308.4	31.3	6.6	0.4	10.0	ND	ND	ND	ND	ND	0.58%	8.93
S18-1	3048.0	285903.1	1.2	0.1	0.1	2.0	ND	ND	ND	ND	ND	0.54%	8.78
S18-2	10.3	1882.5	0.6	1.7	0.3	0.2	ND	ND	ND	ND	ND	0.43%	9.12
S19-1	495.5	30093.5	4.5	0.8	0.04	1.3	ND	ND	ND	ND	0.2	0.57%	8.98
S19-2	29.4	9072.3	0.8	0.2	0.2	0.04	ND	ND	ND	ND	ND	0.73%	8.40
S20-1	179.0	2011.0	138.8	6.6	0.5	12.5	ND	ND	ND	0.4	0.5	0.62%	8.47
S20-2	17.3	598.7	68.5	59.6	0.1	22.2	ND	0.2	0.4	1.2	1.3	0.70%	8.32
S21-1	50.0	11717.2	5.0	6.7	0.1	5.5	ND	ND	ND	ND	ND	0.42%	8.27
S21-2	4.1	235.1	2.1	1.0	0.1	2.8	ND	ND	ND	ND	ND	0.27%	8.86
S22-1	61926.1	13283014.4	135.9	40.6	0.1	23.6	ND	ND	0.1	0.6	0.6	0.46%	8.50
S22-2	387.1	92915.7	59.2	51.8	0.4	69.2	ND	0.1	0.1	0.4	1.3	0.74%	8.02
S23-1	194.3	74170.1	79.8	5.4	0.1	6.6	ND	ND	ND	ND	0.3	0.92%	8.18
S23-2	20.2	5064.4	19.7	0.3	0.03	0.8	ND	ND	ND	ND	ND	0.60%	8.63

Continued

	TBBPA-BAE	TBBPA-BDBPE	TBBPA	TBBPA-MAE	TBBPA-MBAE	TBBPA-MDBPE	TBBPA-MHEE	TBBPA-MDHPE	TBBPA-MHPE	TBBPA-MGE	TBBPA-MBHPE	TOC	PH
S24-1	8132.2	3086140.5	6628.1	727.1	2.2	987.0	13.7	20.4	18.1	25.9	85.0	0.90%	7.81
S24-2	1607.8	524651.8	26.6	42.9	0.1	89.9	ND	0.2	0.3	1.0	4.0	0.71%	8.63
S25-1	20270.3	4634018.1	4021.8	913.2	1.9	800.1	10.4	17.5	14.9	64.4	78.5	0.45%	8.44
S25-2	9367.0	1854155.3	3852.8	293.7	1.6	303.5	0.1	2.0	0.2	3.7	14.5	0.89%	8.07
S26-1	3057.0	743373.6	407643.1	475.2	21.3	1233.6	ND	0.01	178.8	ND	ND	0.49%	8.40
S26-2	70.8	24717.2	37704.5	129.4	2.7	125.8	0.2	ND	ND	1.5	1.4	0.50%	8.23
S27-1	5973.4	874815.1	205.8	29.6	0.7	42.0	ND	ND	0.1	1.4	0.3	0.41%	8.31
S27-2	1247.9	637692.5	112.0	4.1	0.2	7.2	ND	ND	ND	0.1	0.4	0.81%	7.84
S28-1	4480.0	656660.4	302.5	115.6	0.1	48.2	0.4	1.2	1.0	5.1	4.5	0.63%	8.31
S28-2	2455.3	520014.0	0.4	2.3	0.04	0.8	ND	ND	ND	0.2	ND	2.28%	7.65
S29-1	3345.7	535754.9	780.9	216.7	0.2	71.5	0.5	3.8	3.1	15.6	11.5	1.58%	7.91
S29-2	3278.1	267571.5	87.8	8.9	0.2	3.4	ND	ND	ND	ND	0.6	0.21%	8.37
S30-1	4157.1	925566.5	1217.5	151.2	0.2	88.1	0.7	3.0	2.4	14.4	11.3	1.07%	7.86
S30-2	1852.2	132824.5	60.9	5.3	0.2	4.0	ND	ND	ND	0.4	0.4	0.83%	8.39
S31-1	7366.0	1152208.8	19.7	1.9	0.2	4.8	ND	ND	ND	ND	ND	1.07%	8.28
S31-2	30.0	2231.3	1.5	3.2	0.3	1.6	ND	ND	ND	ND	0.2	0.58%	8.13
S32-1	26.4	364.7	13.1	0.1	0.1	2.2	ND	ND	ND	ND	ND	0.37%	8.85
S32-2	3.1	ND	1.9	ND	0.2	ND	ND	ND	ND	ND	ND	0.88%	8.28
S33-1	247.5	18729.1	5.4	6.0	0.04	2.3	ND	ND	ND	ND	0.2	0.42%	8.43
S33-2	149.1	15830.2	4.1	2.6	0.04	1.4	ND	ND	ND	ND	0.2	0.50%	8.52
S34-1	3029.4	985168.2	845.9	99.0	0.2	61.3	ND	ND	ND	0.6	1.5	1.70%	8.43
S34-2	1091.7	568425.6	330.5	559.4	0.3	82.9	1.0	5.2	5.1	42.4	29.8	0.10%	8.26
S35-1	768.3	66188.2	15.7	0.1	0.1	0.6	ND	ND	ND	ND	ND	0.60%	8.73
S35-2	4.1	393.0	11.7	2.1	0.4	0.4	ND	ND	ND	ND	ND	0.57%	8.88
S36-1	162.3	9826.7	67.3	66.5	0.1	2.8	ND	ND	0.1	1.1	1.3	0.26%	9.08
S36-2	7.5	ND	30.6	42.0	0.05	1.4	ND	ND	ND	0.4	1.0	0.24%	8.67
S37-1	480.9	90928.5	6930.6	1344.6	0.4	313.7	1.9	6.6	5.8	19.9	36.2	0.58%	9.47
S37-2	2.0	ND	20.2	4.3	0.1	2.3	ND	ND	ND	ND	ND	0.41%	9.35
S38-1	4183.8	880374.8	388.6	41.5	0.2	28.1	ND	ND	ND	0.3	0.4	1.23%	8.31
S38-2	1195.7	413453.9	297.2	30.6	0.6	11.7	ND	ND	ND	0.4	0.6	2.45%	7.93
S39-1	695.5	18180.9	36.8	0.9	0.1	2.1	ND	ND	ND	ND	ND	0.84%	8.78
S39-2	33.5	9153.6	9.0	4.6	0.6	ND	ND	ND	ND	ND	1.7	0.59%	8.58
S40-1	31.9	11391.6	28.3	ND	ND	ND	ND	ND	ND	ND	ND	2.19%	7.80
S40-2	12.2	4656.3	ND	0.6	0.04	1.5	ND	ND	ND	ND	ND	0.75%	8.18
S41-1	44.0	4302.3	0.3	0.8	0.2	7.1	ND	ND	ND	ND	ND	0.92%	8.00
S41-2	2.6	336.9	0.1	0.2	0.1	3.5	ND	ND	ND	ND	ND	0.17%	8.52
S42-1	27.2	2110.1	39.4	0.1	0.3	1.1	ND	ND	ND	ND	ND	1.02%	8.05
S42-2	9.1	ND	28.3	0.1	0.03	0.4	ND	ND	ND	ND	ND	0.81%	7.99

[a]SX-1 means the top lay soil, SX-2 means the sub-layer soil; TOC was determined with O.I. analytical solids TOC analyzer (O.I. Analytical, USA). A Thermo Orion 3 Star pH Benchtop meter was used to measure the pH value. The detailed procedures about the TOC and pH detection were described somewhere.[3]

Table S5. Spearman's rank correlation test results.

		TBBPA-BAE	TBBPS-BDBPE	TBBPA	TBBPA-MAE	TBBPA-MBAE	TBBPA-MDBPE	TOC
TBBPA-BDBPE	Correlation Coefficient	0.928						
	Sig. (2-tailed)	<0.05						
TBBPA	Correlation Coefficient	0.598	0.632					
	Sig. (2-tailed)	<0.05	<0.05					
TBBPA-MAE	Correlation Coefficient	0.620	0.690	0.800				
	Sig. (2-tailed)	<0.05	<0.05	<0.05				
TBBPA-MBAE	Correlation Coefficient	0.641	0.465	0.455	0.396			
	Sig. (2-tailed)	<0.05	<0.05	<0.05	<0.05			
TBBPA-MDBPE	Correlation Coefficient	0.545	0.646	0.752	0.857	0.419		
	Sig. (2-tailed)	<0.05	<0.05	<0.05	<0.05	<0.05		
TOC	Correlation Coefficient	0.291	0.373	0.325	0.277	0.069	0.355	
	Sig. (2-tailed)	<0.05	<0.05	<0.05	<0.05	0.533	<0.05	
PH	Correlation Coefficient	-0.117	-.205	-0.284	-0.186	0.017	-0.280	-0.494
	Sig. (2-tailed)	0.290	0.061	<0.05	0.091	0.877	<0.05	<0.05

Table S6. Mass chromatography peack area ratios of untargeted TBBPA analogs compared to TBBPA in soil samples.

	TBBPA-MME/TBBPA	TriBBPA-MAE/TBBPA	DBBPA-MAE/TBBPA	TriBBPA/TBBPA	DBBPA/TBBPA
S1-1	2.89%	0.22%	ND	9.80%	0.07%
S1-2	0.28%	ND	ND	0.32%	ND
S2-1	3.70%	0.25%	ND	14.00%	0.35%
S2-2	3.32%	ND	ND	3.65%	ND
S3-1	3.85%	ND	ND	2.05%	ND
S3-2	1.23%	ND	ND	0.53%	ND
S4-1	5.42%	ND	ND	0.70%	ND
S4-2	0.11%	ND	ND	0.22%	ND
S5-1	7.64%	1.70%	0.99%	13.92%	4.87%
S5-2	9.01%	3.00%	3.03%	8.91%	5.01%
S6-1	11.87%	ND	ND	1.69%	0.09%
S6-2	10.65%	ND	ND	1.89%	ND
S7-1	25.67%	ND	ND	0.88%	ND
S7-2	9.46%	ND	ND	3.45%	ND
S8-1	6.32%	ND	ND	1.17%	ND
S8-2	23.52%	ND	ND	0.40%	ND
S9-1	10.74%	ND	ND	0.64%	ND
S9-2	12.02%	ND	ND	0.26%	ND
S10-1	28.47%	0.42%	0.003%	5.09%	0.15%
S10-2	4.36%	ND	ND	ND	ND
S11-1	7.82%	0.35%	ND	4.39%	0.04%
S11-2	3.18%	ND	ND	0.52%	0.14%
S12-1	16.88%	0.47%	ND	4.18%	0.06%
S12-2	11.18%	ND	ND	0.61%	ND
S13-1	3.05%	ND	0.02%	2.81%	0.02%
S13-2	0.44%	ND	ND	2.21%	ND
S14-1	2.40%	ND	ND	1.96%	ND
S14-2	2.03%	ND	ND	1.37%	ND
S15-1	6.17%	ND	ND	2.62%	ND
S15-2	2.63%	ND	ND	1.13%	ND
S16-1	3.16%	2.31%	0.09%	25.80%	0.98%
S16-2	9.17%	1.12%	ND	5.68%	0.14%
S17-1	0.80%	ND	ND	5.02%	ND
S17-2	0.69%	ND	ND	1.18%	ND
S18-1	0.55%	ND	ND	ND	ND
S18-2	27.42%	ND	ND	ND	ND
S19-1	182.50%	ND	ND	1.95%	0.77%
S19-2	13.86%	ND	ND	ND	ND
S20-1	5.19%	ND	0.04%	1.98%	0.06%
S20-2	23.40%	1.98%	0.22%	3.44%	0.25%
S21-1	29.27%	ND	12.18%	5.30%	2.74%
S21-2	4.62%	ND	1.70%	0.10%	ND
S22-1	85.09%	3.46%	1.11%	2.12%	0.29%
S22-2	21.70%	1.68%	0.69%	3.16%	0.17%

Continued

	TBBPA-MME/TBBPA	TriBBPA-MAE/TBBPA	DBBPA-MAE/TBBPA	TriBBPA/TBBPA	DBBPA/TBBPA
S23-1	12.06%	ND	ND	2.17%	0.15%
S23-2	2.37%	ND	ND	0.29%	ND
S24-1	12.51%	1.10%	0.08%	7.07%	0.35%
S24-2	32.49%	8.98%	0.60%	6.12%	1.08%
S25-1	4.78%	1.56%	0.29%	12.20%	0.27%
S25-2	0.80%	0.23%	0.05%	3.83%	0.06%
S26-1	2.63%	ND	ND	1.68%	0.02%
S26-2	1.83%	0.01%	0.00%	4.31%	0.09%
S27-1	24.59%	ND	ND	2.59%	0.16%
S27-2	3.41%	ND	ND	0.65%	0.01%
S28-1	17.37%	1.12%	ND	3.55%	0.15%
S28-2	1.46%	0.14%	ND	3.34%	0.00%
S29-1	7.44%	1.41%	0.02%	6.60%	0.31%
S29-2	1.89%	ND	ND	4.10%	0.08%
S30-1	8.43%	0.57%	0.04%	4.75%	0.60%
S30-2	4.50%	0.66%	ND	3.70%	0.10%
S31-1	20.32%	ND	ND	0.58%	ND
S31-2	11.68%	ND	ND	3.69%	4.67%
S32-1	0.47%	ND	ND	0.58%	ND
S32-2	1.43%	ND	ND	ND	ND
S33-1	18.47%	ND	ND	4.58%	0.11%
S33-2	12.43%	ND	ND	2.51%	ND
S34-1	4.50%	0.58%	ND	7.20%	0.32%
S34-2	6.25%	ND	ND	4.93%	0.05%
S35-1	1.18%	ND	ND	ND	ND
S35-2	23.71%	ND	ND	0.82%	ND
S36-1	12.69%	2.92%	ND	3.36%	0.34%
S36-2	16.71%	3.87%	ND	3.15%	ND
S37-1	3.32%	0.74%	0.19%	5.87%	0.12%
S37-2	15.62%	ND	ND	1.26%	0.06%
S38-1	7.34%	ND	ND	1.27%	ND
S38-2	4.55%	ND	ND	5.04%	ND
S39-1	20.18%	ND	ND	1.54%	ND
S39-2	6.04%	ND	ND	1.18%	ND
S40-1	ND	ND	ND	ND	ND
S40-2	1.84%	ND	ND	0.43%	0.01%
S41-1	31.23%	ND	ND	ND	ND
S41-2	10.94%	ND	ND	0.61%	ND
S42-1	4.24%	ND	ND	ND	ND
S42-2	0.77%	ND	ND	0.31%	ND

Table S7. Calculated physical-chemical constants[a] of TBBPA, TBBPA derivatives and potential transformation products.

	WS[b]	log K_{ow}[c]	log K_{aw}[d]	log K_{oa}[e]	log K_{oc}[f]	BCF[g]
TBBPA-BDBPE	1.2E-10	11.5	-8.8	20.3	7.4	81
TBBPA-BAE	3.1E-07	10.0	-5.3	15.3	6.6	442
TBBPA-BHEE	1.6E-04	6.8	-11.1	17.9	4.0	7720
TBBPA-BGE	3.3E-05	7.4	-10.3	17.7	5.0	8428
TBBPA-MDBPE	6.9E-07	9.4	-9.9	19.3	6.3	928
TBBPA-MBAE	4.8E-06	9.0	-8.9	17.9	6.1	1388
TBBPA-MAE	3.5E-05	8.6	-8.2	16.8	5.9	2163
TBBPA--MGE	3.5E-04	7.3	-10.9	18.2	5.1	9440
TBBPA-MHEE	3.8E-03	6.8	-12.6	19.4	4.5	7793
TBBPA-MHPE	1.2E-03	7.3	-12.5	19.7	5.0	5380
TBBPA-MDHPE	1.2E-03	6.6	-13.9	20.4	3.9	5405
TBBPA-MBHPE	2.1E-04	7.6	-13.4	21.0	5.1	3964
TriBBPA-MAE	6.5E-04	7.7	-7.8	15.5	5.4	5905
HTriBBPA-MAE	1.3E-03	7.2	-11.7	19.0	5.3	10150
DBBPA-MAE	1.2E-02	6.8	-7.4	14.2	4.9	14910
TBBPA	1.0E-03	7.2	-11.0	18.2	5.2	10580
TriBBPA	1.9E-02	6.3	-10.6	16.9	4.7	6797
DBBPA	0.3	5.4	-10.2	15.6	4.3	1758
MBBPA	5.7	4.5	-9.8	14.4	3.8	455
BPA	172.7	3.6	-9.1	12.8	3.1	72

[a]Calculated by US EPA Suite V 4.1;

[b]Water solubility, (mg/L);

[c]octanol-water partition coefficient;

[d]air-water partition coefficient;

[e]octanol-air partition coefficient;

[f]soil absorption coefficient;

[g]bioconcentration factor (L/kg, wet-wt).

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