Supplementary Materials

Occurrence and distribution of several endocrine disrupting chemicals in a chemical park: Exploring for health risks of multiple pollutants

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Supplementary Text 1. Chemical analysis

For TCC, TCS, parabens, BPAs, and TBBPAs, they were analyzed with an Exion LC AD Series UPLC system connected to an API 5500 triple-quadrupole MS/MS system (AB Sciex, Framingham, MA, USA). An analytical column (BEH C18, 100mm × 2.1mm, 1.7 μm; Waters), connected to a BEH C18 guard column (5 mm × 2.1 mm, 1.7 μm; Waters) was used for chromatographic separation. The column temperature was maintained at 40 °C. A gradient mobile phase of Milli-Q water that contained 2mM ammoniumacetate (A) and methanol (B) was used. The flow rate and the sample injection volume were 0.3 mL/min and 5.0 μL, respectively. The gradient condition was as follows: held at 25% B for 1.00 min; increased to 60% B in 1.50 min, held at 60% B for 2.00 min; increased to 99% B in 2.00 min, held at 99% B for 3.00 min; and then returned to initial conditions (25% B) and equilibrated for additional 1.50 min. Target analytes were detected using multiple reaction monitoring (MRM) in negative ion electrospray mode. The MRM transitions of ions monitored are listed in Table S2. Nitrogen was used as curtain gas and collision gas. The curtain gas, collision gas, ion spray voltage and desolvation temperature were 35 psi, 9 psi, -4500 V and 550 °C, respectively.

For PAEs, they were analyzed using a Thermo Scientific TRACE 1300 Series gas chromatograph interfaced with a Thermo Scientific TSQ 8000 Evo triple quadrupole mass spectrometer (GC-MS/MS; Thermo Fisher Scientific, San Jose, CA, USA). The analytes were separated using a capillary column (TG-5MS, 30 m × 0.25 mm × 0.25 μm; Thermo Fisher Scientific) and ultra-high purity helium gas (purity 99.999%) was used as a mobile phase with the flow rate of 1.0 mL/min. Argon was used as the collision gas. The initial oven temperature was set at 60 °C (held for 1.0 min), ramped to 220 °C at a rate of 20 °C/min, and final ramped to 290 °C at 5 °C/min (held for 3.0 min). The ion source, transmission line, and injector were held

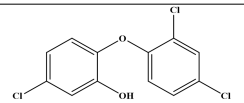
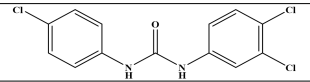
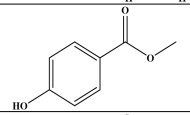
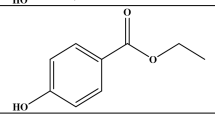
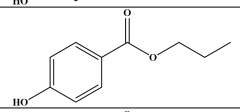
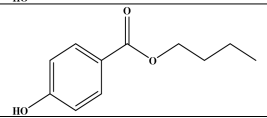
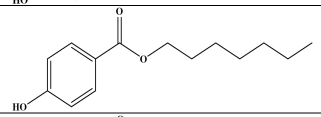
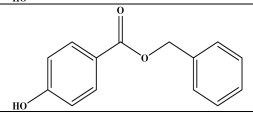
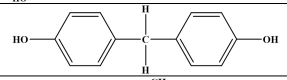
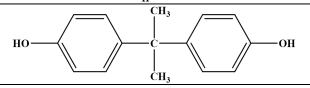
at a constant temperature of 300 °C, 300 °C and 250 °C, respectively. Target analytes were identified and quantified based on the retention time, the most abundant signature m/z ion (quantitative ion), the second most abundant m/z ion (qualitative ion), and their ratio by using selective ion-monitoring (SIM) mode.

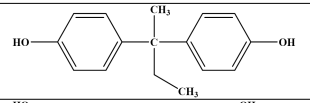
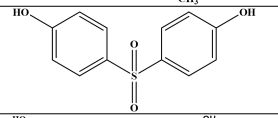
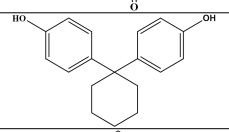
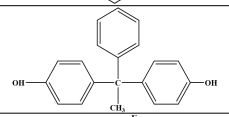
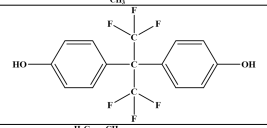
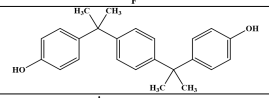
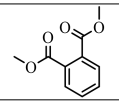
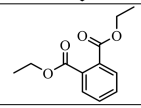
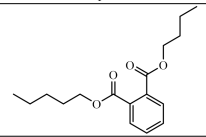
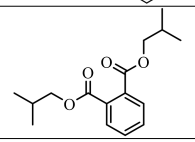
Supplementary Table 1. Sampling information of soil and sediment

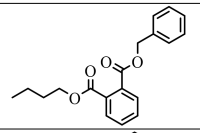
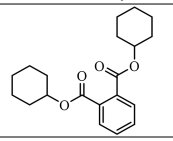
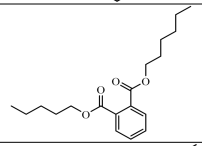
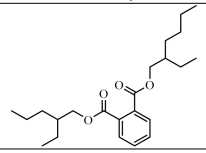
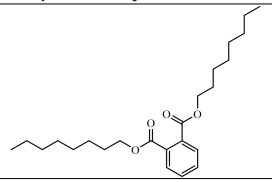
Sampling number	Latitude	Longitude	Soil types	Description
Soil				
S1	120°59′42.62″	32°31′02.97″	soil along a canal (Canal Soil)	The site is located close to the Bingcha Canal and 5 km from the chemical park. It is located in a busy river transportation area at which human activities are frequent.
S2	121°03′20.63″	32°32′41.67″	soil from a wastewater treatment plant (WWTP Soil)	The site is near a wastewater treatment plant in the chemical park.
S3	121°03′20.70″	32°32′44.32″	WWTP Soil	The site is near a wastewater treatment plant in the chemical park.
S4	121°03′19.12″	32°32′42.96″	WWTP Soil	The site is near a wastewater treatment plant in the chemical park.
S5	121°03′25.35″	32°32′48.35″	WWTP Soil	The site is near a wastewater treatment plant in the chemical park.
S6	121°02′23.05″	32°33′32.30″	Canal Soil	The site is near the point where the Bingcha Canal enters the sea.
S7	121°04′35.14″	32°32′41.39″	soil from a roadside (Road Soil)	The site is near a chemical production enterprise specializing in the production of plant protection agents.
S8	121°03′10.50″	32°29′46.12″	Canal Soil	The site is near the point where the Bingcha Canal enters the sea.
S9	121°03′21.21″	32°31′34.87″	Road Soil	-
S10	121°03′10.03″	32°32′43.94″	Road Soil	-
S11	121°00′52.47″	32°32′13.30″	Road Soil	-
S12	121°00′58″	32°32′19″	Road Soil	-
S13	121°02′04.31″	32°32′27.69″	Road Soil	-
S14	121°02′14.97″	32°32′08.01″	Road Soil	-
S15	121°02′23.36″	32°31′48.07″	Road Soil	The site is near a chemical enterprise.
S16	121°02′46.65″	32°31′56.24″	Road Soil	The site is near a chemical production enterprise specializing in the production of inorganic fluorine series products.
S17	121°03′15.30″	32°32′04.18″	Road Soil	The site is near a chemical enterprise.

S18	121°03′02.61″	32°32′27.71″	Road Soil	-
S19	121°02′39.30″	32°32′18.08″	Road Soil	The site is near a manufacturer of pharmaceutical intermediates.
S20	121°02′30.81″	32°32′38.56″	Road Soil	The site is near a manufacturer of fertilizer production.
Sediment				
S21	121°03′22.99″	32°32′46.70″		sediment from a pond outside the park
S22	121°03′30.56″	32°31′58.33″		sediment from a river in the chemical park
S23	121°01′52.35″	32°32′34.58″		sediment from a river in the chemical park

Supplementary Table 2. Select physicochemical properties and molecular structures of target analytes

Target analyte	Molecular formula	CAS	MW	Log K_{oc}[a]	Log K_{ow}[b]	Molecular structure
triclosan (TCS)	$C_{12}H_7Cl_3O_2$	3380-34-5	289.54	4.265	4.66	
triclocarban (TCC)	$C_{13}H_9Cl_3N_2O$	101-20-2	315.58	3.732	4.90	
methyl paraben (MeP)	$C_8H_8O_3$	99-76-3	152.15	2.099	2.00	
ethyl paraben (EtP)	$C_9H_{10}O_3$	120-47-8	166.17	2.365	2.49	
propyl Paraben (PrP)	$C_{10}H_{12}O_3$	94-13-3	180.08	2.631	2.98	
butyl paraben (BuP)	$C_{11}H_{14}O_3$	94-26-8	194.23	2.896	3.47	
heptyl paraben (HepP)	$C_{14}H_{12}O_3$	1085-12-7	236.30	3.694	4.94	
benzyl paraben (BzP)	$C_{14}H_{20}O_3$	94-18-8	228.24	3.703	3.70	
4,4'-methylenediphenol (BPF)	$C_{13}H_{12}O_2$	620-92-8	200.23	4.472	3.06	
2,2-bis(4-hydroxyphenyl)propane (BPA)	$C_{15}H_{16}O_2$	80-05-7	228.29	4.876	3.64	

2,2-bis(4-hydroxyphenyl)butane (BPB)	$C_{16}H_{18}O_2$	77-40-7	242.31	5.174	4.13	
4-hydroxyphenyl sulfone (BPS)	$C_{12}H_{10}O_4S$	80-09-1	250.27	3.882	1.65	
4,4'-cyclohexylidenebisphenol (BPZ)	$C_{18}H_{20}O_2$	843-55-0	268.35	5.784	5.00	
4,4'-(1-phenylethylidene)bisphenol (BPAP)	$C_{20}H_{18}O_2$	1571-75-1	290.36	6.261	4.86	
4,4'-hexafluoroisopropylidene)diphenol (BPAF)	$C_{15}H_{10}F_6O_2$	1478-61-1	336.23	6.205	4.47	
4,4'-(1,4-phenylenediisopropylidene)bisphenol (BPP)	$C_{24}H_{26}O_2$	2167-51-3	346.46	7.115	6.25	
dimethyl phthalate (DMP)	$C_{10}H_{10}O_4$	131-11-3	194.19	1.68	1.60	
diethyl phthalate (DEP)	$C_{12}H_{14}O_4$	84-66-2	222.24	2.13	2.47	
di-*n*-butyl phthalate (DBP)	$C_{16}H_{22}O_4$	84-74-2	278.35	3.28	4.90	
di-iso-butyl phthalate (DIBP)	$C_{16}H_{22}O_4$	84-69-5	278.35	3.07	4.11	

benzyl butyl phthalate (BzBP)	$C_{19}H_{20}O_4$	85-68-7	312.37	3.41	4.73	
dicyclohexyl phthalate (DCHP)	$C_{20}H_{26}O_4$	84-61-7	330.42	4.25	6.20	
di-*n*-hexyl phthalate (DNHP)	$C_{20}H_{30}O_4$	84-75-3	334.46	4.23	6.82	
di-*n*-octyl phthalate (DNOP)	$C_{24}H_{38}O_4$	117-84-0	390.56	5.27	7.50	
bis(2-ethylhexyl) phthalate (DEHP)	$C_{24}H_{38}O_4$	117-81-7	390.56	5.00	8.01	

[a]Corrected Log soil adsorption coefficient estimated from Log K_{ow} values using the US Environmental Protection Agency's EPISuite™, [KOCWIN v1.67].
[b]Log octanol-water partition coefficient (25 °C) estimated using the US Environmental Protection Agency's EPISuite™, [KOWWIN v1.66].

Supplementary Table 3. Optimized UPLC-MS/MS and GC-MS/MS parameters for analysis of target analytes

Target analytes	MRM transition for quantification	MRM transition for confirmation	DP[a] (V)	CE[b] (eV)	EP[c] (V)	CXP[d] (V)	DW[e] (ms)
UPLC-MS/MS							
TCC	315.0 > 162.0	315.0 > 126.0	-60	-20/-32[f]	-10	-5/-7	40
TCS	289.0 > 35.0	-	-30	-25	-10	-8	40
MeP	150.9 > 92.0	150.9 > 136.0	-40	-28	-10	-9	40
EtP	165.0 > 92.0	165.0 > 136.0	-30	-30	-10	-5	40
PrP	179.0 > 92.0	179.0 > 136.0	-30	-35	-10	-7	40
BuP	193.0 > 92.0	193.0 > 136.0	-22	-30	-10	-10	40
HepP	235.0 > 92.0	235.0 > 136.0	-30	-27	-10	-5	40
BzP	226.9 > 92.0	226.9 > 136.1	-30	-30	-10	-10	40
BPF	199.0 > 93.0	199.0 > 105.0	-130	-28	-10	-17	40
BPA	227.0 > 212.0	227.0 > 133.0	-129	-26/-30	-10	-17	40
BPB	241.0 > 212.0	241.0 > 147.0	-120	-38	-10	-17	40
BPS	249.0 > 92.0	249.0 > 108.0	-150	-44/-36	-10	-17	40
BPZ	267.0 > 173.0	267.0 > 145.0	-170	-38/-54	-10	-17	40
BPAP	289.0 > 274.0	289.0 > 211.0	-159	-28/-38	-10	-17	40
BPAF	335.0 > 265.0	335.0 > 69.0	-140	-29/-71	-10	-17	40
BPP	345.0 > 330.0	345.0 > 133.0	-180/-100	-36/-39	-10	-17/-14	40
TCBPA	365.0 > 314.0	365.0 > 286.0	-170	-38/-45	-10	-17	40
TBBPA	542.8 > 418.0	542.8 > 446.0	-183	-55/-43	-10	-17	40
TBBPS	564.0 > 485.0	564.0 > 250.0	-150	-48/-58	-10	-17	40

GC-MS/MS							
DMP	163.0 > 77.0	163.0 > 133.0	-	20/10	-	-	-
DEP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-
DIBP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-
DBP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-
DNHP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-
BzBP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-
DCHP	167.0 > 65.0	167.0 > 121.0	-	30/20	-	-	-
DEHP	167.0 > 65.0	167.0 > 121.0	-	30/20	-	-	-
DNOP	149.0 > 65.0	149.0 > 93.0	-	20/15	-	-	-

[a]DP: declustering potential; [b]CE: collision energy; [c]EP: entrace potential; [d]CXP: collision cell exit potential; [e]DW: dwell time; [f]: two values for quantification and confirmation MRM transitions, respectively.

Supplementary Table 4. Recoveries, limits of detection (LODs), and limits of quantitation (LOQs) for target EDCs in this study

Target compounds	Recoveries (%, mean)	LODs (μg kg^{-1})	LOQs (μg kg^{-1})
TCS	63.9	0.411	1.37
TCC	55.1	0.0034	0.0113
MeP	102	0.370	1.23
EtP	111	0.0335	0.112
PrP	103	0.0866	0.289
BuP	109	0.0215	0.0718
HepP	65.3	0.0118	0.0394
BzP	127	0.0691	0.230
BPF	96.4	0.510	1.70
BPA	105	0.468	1.56
BPB	97.1	0.735	2.45
BPS	95.7	0.0306	0.102
BPZ	96.4	0.137	0.457
BPAP	126	0.135	0.452
BPAF	95.5	0.0111	0.0370
BPP	71.8	0.0609	0.203
TCBPA	148	0.239	0.795
TBBPA	80.2	0.272	0.907
TBBPS	49.6	0.321	1.07
DMP	91.0	0.0051	0.0170
DEP	82.2	0.0005	0.0018
DIBP	91.5	0.0002	0.0005
DBP	110	0.0001	0.0004
DNHP	81.0	0.0001	0.0004
BzBP	82.3	0.0051	0.0169
DCHP	83.1	0.0069	0.0230
DEHP	90.1	0.0022	0.0072
DNOP	78.9	0.0480	0.160

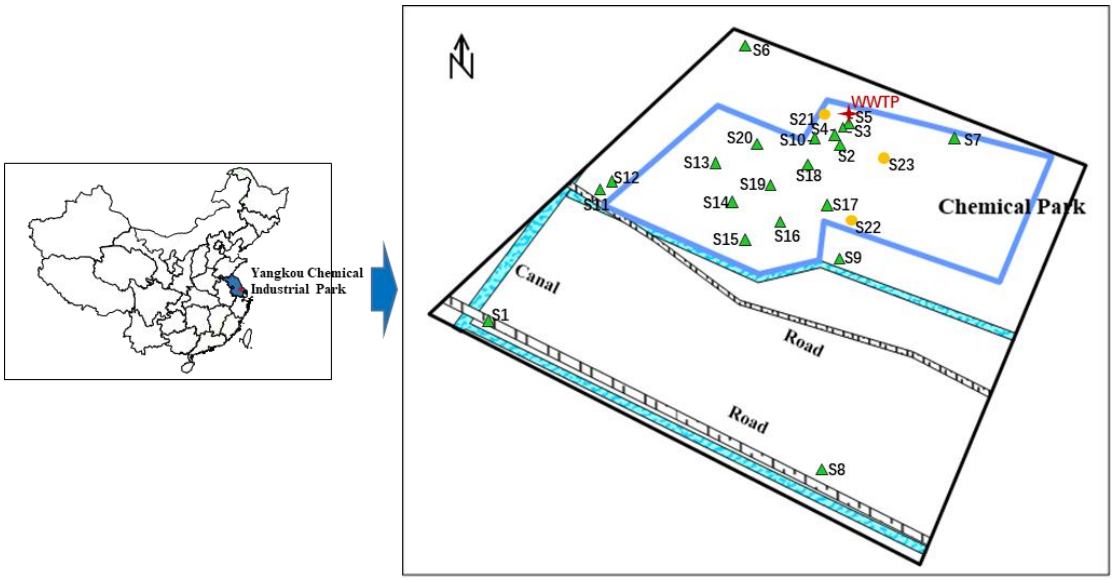
Supplementary Table 5. Parameters used for health risk assessment[1].

Parameters	**Unit**	**Adults**
Soil ingestion rate (*IRS*)	mg day^{-1}	100
Exposure frequency (*EF*)	days $year^{-1}$	350
Exposure duration (*ED*)	year	24
Unit conversion factor (*CF*)	kg mg^{-1}	10^{-6}
Body weight (*BW*)	kg	70
Average time (*AT*)	days	Non-carcinogenic risk: 365 ×*ED*
Respiratory rate (*Ij*)	m^3 day^{-1}	13.5
Particulate emission factor (*PEF*)	m^3 kg^{-1}	1.36×10^9
Dermal exposure area (*SA*)	cm^2	5700
Soil adherence factor (*AF*)	mg cm^{-2} day^{-1}	0.07
Dermal adsorption fraction (*ABS*)	unitless	0.1

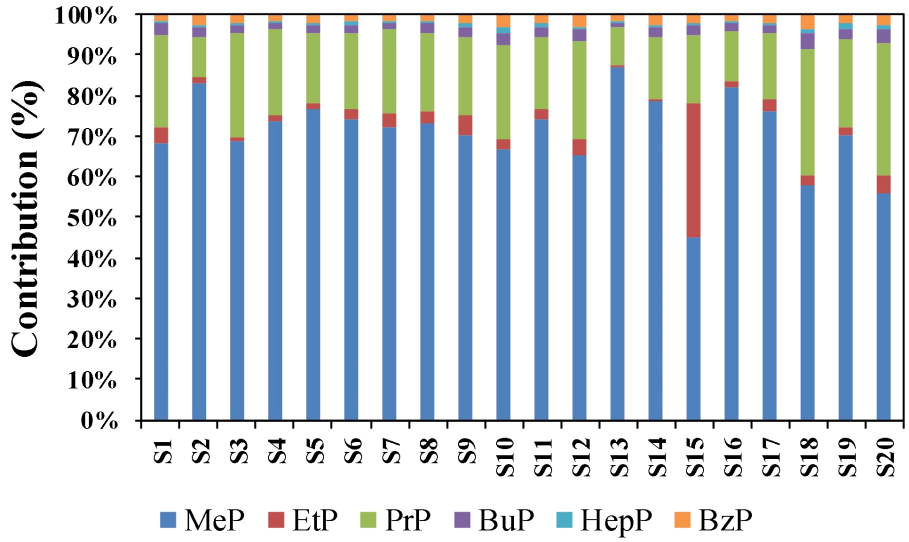
Supplementary Table 6. Concentrations of EDCs in soil from different sampling sites

Sampling site	∑(TCS + TCC)	$\sum_6$parabens	$\sum_8$BPAs	$\sum_3$TBBPAs	$\sum_9$PAEs
S1	145	39.9	29.7	1.28	428
S2	130	23.4	30.3	11.7	388
S3	128	29.7	54.6	3.35	271
S4	144	34.1	33.9	20.0	283
S5	136	27.0	34.6	154	431
S6	129	30.1	51.9	2.20	312
S7	144	32.8	35.9	3.03	349
S8	145	34.6	35.2	2.40	661
S9	168	24.6	38.0	7.43	375
S10	151	18.6	33.9	3.31	288
S11	149	25.3	58.6	6.13	499
S12	156	20.8	33.7	3.95	259
S13	152	31.8	47.9	0.86	224
S14	156	21.5	30.2	5.18	250
S15	127	24.5	36.5	<LOQ[a]	196
S16	139	25.9	21.2	3.34	295
S17	131	23.8	31.6	5.19	222
S18	159	17.5	28.4	3.20	261
S19	186	24.5	31.6	24.1	264
S20	150	22.0	35.4	2.61	

[a]<LOQ: Below the limit of quantitation



Supplementary Figure 1. The sampling sites around the Yangkou Chemical Industrial Park.



Supplementary Figure 2. The composition profiles of parabens in soils.

Reference:

1. Tao H, Wang Y, Liang H, et al. Pollution characteristics of phthalate acid esters in agricultural soil of Yinchuan, northwest China, and health risk assessment. *Environ Geochem Health* 2020;42:4313-26.