SUPPLEMENTARY INFORMATION

Presence of novel and legacy flame retardants and other pollutants in an e-waste site in China and associated risks.

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Section S1. Chemicals and reagents

Standard solutions of triethyl phosphate (TEP), tri-isopropyl phosphate (TiPP), tri-n-propylphosphate (TnPP), tri-n-butyl phosphate (TNBP), tri(2-chloroethyl) phosphate (TCEP), tri(2-chloro-isopropyl) phosphate (TCIPP), tri(2-chloro,1-chloromethy-ethyl) phosphate (TDCIPP), tri(2-ethylhexyl) phosphate (TEHP), 2-ethylhexyl diphenyl phosphate (EHDPP), tri-phenyl phosphate (TPHP), and tricresyl phosphates (TCP) were purchased from AccuStandard (New Haven, CT, USA).

PBDEs solutions containing congeners 28, 47, 66, 85, 99, 100, 138, 153 and 154 at 10 µg/mL in isooctane, BDE-183 at 50 µg/mL in isooctane and BDE-209 at 50 µg/mL in isooctane:toluene (1:1) were also provided by AccuStandard.

For OCP and PCB analysis, Pesticide Mix 1 was purchased from AccuStandard. It contains the following compounds: aldrin, dieldrin, endrin, isodrin, α-, β-, γ- and δ- HCHs, cis- and trans- chlordane, 2,4′-DDD, 2,4′-DDE, 2,4′-DDT, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, α- and β-endosulfan, heptachlor, heptachlor exo- and endo-epoxides, hexachlorobenzene (HCB), methoxychlor, mirex, and oxychlordane, at a concentration of 10 µg/mL and the PCB congeners 28, 52, 101, 138, 153 and 180, at 1 µg/mL in toluene. Dicofol at a concentration of 100 µg/mL in methanol, endosulfan sulphate (100 µg/mL in methanol), hexachlorobutadiene (HCBu) (2 mg/mL in methanol) and pentachlorobenzene (solid, 98% purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Section S2. Instrumental analysis

For OPEs, 1 µL was injected in pulsed splitless mode at 250°C. The temperature gradient started at 90°C (1 min hold time), increased to 220°C at 10°C/min, to 240°C at 20°C/min, to 280°C at 5°C/min (5 min), and finally to 325°C at 30°C/min (5 min hold time), with a total run time of 35 min. The ion source temperature was set at 280ºC.

For OCPs and PCBs analysis, 1 µL was injected in pulsed splitless mode at 250ºC. The temperature gradient was set at 70°C (1 min hold time), increased to 175°C at 6°C/min (4 min hold time), to 235°C at 3°C/min, to 315°C at 7°C/min (10 min hold time), with a total run time of 64 min. The ion source temperature was set at 225°C.

For PBDEs, the oven temperature was set at 100°C, increased to 250°C at 10°C/min, to 310°C at 15°C/min (15 min hold time) and the total run time was of 36 min. 1 µL of sample was injected in pulsed splitless mode with the injector temperature set at 300ºC. The MS ion source worked at 250ºC. For spectrometry detection, selected ion monitoring (SIM) mode was used. Ions with mass charge ratio (m/z) of 79 were monitored for all PBDEs except for BDE 209 where m/z of 486.5 was used for quantification. For confirmation purposes, m/z 81 and 161 were used.

Table S1. Sediment, water and soil samples collected in the Baihe e-waste site, identification codes, GPS coordinates and water content of sediments and soils.

SAMPLES	CODE	GPS location		Water content (%)
POLLUTED POND (POND 1)	PLAS	N23º35´28.18"	E113º01´31.88"	17.2
	SED1	N23º35´28.18"	E113º01´31.88"	51.9
	WAT1	N23º35´28.18"	E113º01´31.88"	
	SOIL1	N23º35´34.26"	E113º01´32.45"	31.8
	SOIL2	N23º35´34.47"	E113º01´32.65"	14.1
	SOIL3	N23º35´34.47"	E113º01´32.65"	12.6
POND 2	SED2	N23º35´47.64"	E113º01´34.23"	31.6
	WAT2	N23º35´47.64"	E113º01´34.23"	
	SOIL4	N23º35´47.48"	E113º01´37.27"	19.6
POND 3	SED3	N23º35´48.69"	E113º01´35.15"	35.1
POND 4	WAT3	N23º35' 48.30"	E113º01'35.96"	
Irrigation canal	WAT4	N23º35' 28.88"	E113º01'36.01"	
River	WAT5	N23º 35' 35.38"	E113º01'40.34"	

Table S2. Biometric data of individual hen eggs and water and lipid content, in %. First number of the sample name indicates the pooled sample; second number indicates the individual egg.

Sample	Length (mm)	Width (mm)	Weight (g)	Eggshell thickness (mm)	% Water content	% Lipid content
HEN1-1	52.72	42.44	50.99	0.28		
HEN1-2	48.28	37.25	36.56	0.27	74.17	2.28
HEN1-3	53.52	43.07	52.96	0.29		
HEN2-1	54.58	40.55	47.45	0.29		
HEN2-2	56.87	42.95	56.40	0.31	73.40	3.50
HEN2-3	54.81	42.29	53.29	0.28		
HEN3-1	51.50	37.68	40.27	0.23		
HEN3-2	53.74	40.52	46.91	0.20	71.78	4.16
HEN3-3	54.53	43.61	55.46	0.25		
HEN4-1	57.85	42.61	56.30	0.33		
HEN4-2	52.90	40.51	49.13	0.31		
HEN4-3	51.86	40.95	47.22	0.28	72.76	3.50
HEN4-4	56.71	47.84	68.72	0.30		
HEN4-5	53.47	40.65	47.98	0.27		
HEN5-1	53.62	40.51	48.56	0.28		
HEN5-2	54.63	42.50	53.74	0.28		
HEN5-3	50.47	41.63	48.18	0.27	71.46	3.16
HEN5-4	52.20	41.06	48.90	0.26		
HEN5-5	51.26	41.30	47.95	0.29		
HEN6-1	53.05	38.14	42.42	0.27		
HEN6-2	52.53	39.37	42.49	0.24		
HEN6-3	54.45	40.42	48.37	0.27	73.04	3.10
HEN6-4	52.95	39.34	43.63	0.26		
HEN6-5	56.60	39.52	46.01	0.23		
Mean	*53.5±1*	*41.1±2.2*	*49.2±6.5*	*0.27±0.03*	*72.7±1*	*3.3±0.6*

Table S3. OPEs studied, CAS number for unambiguous identification and GC-MS/MS retention times and monitored transitions and collision energies for studied OPEs. Recoveries (% ± standard deviation) and blank contribution indicated in ng/g dw in soil and ng/g ww in eggs and ng/L for water.

Compound	CAS no	Rt (min)	Q1 (CE, eV)	Q2 (CE, eV)	% R±SD Soil	% R±SD Water	% R±SD Eggs	Bk ±SD (ng/g) Soil	Bk ±SD (ng/L) Water	Bk ±SD (ng/g) Eggs
TEP	78-40-0	4.3	155>99 (30)	127>81 (30)	74 ±10	93 ± 9.5	96 ± 9	1.2 ± 2.2	nd	8 ± 7
TiPP (TPP)	513-02-0	5.2	141>81 (30)	183>99 (30)	91 ±2.5	57 ± 1	75 ± 8	8.9 ±13.6	nd	nd
TnPP (TPP)	513-08-6	7.7	141>81 (30)	183>99 (30)	148 ±9	102 ± 26	96 ± 5	nd	nd	nd
TnBP	126-73-8	11.0	155>81 (40)	211>99 (40)	151 ±5	107 ± 6.5	86 ± 20	126 ± 220	4.1 ± 0.6	27 ± 10
TCEP	115-96-8	12.3	249>63 (30)	205>63 (30)	91 ±11	98 ± 1	76 ± 25	58.7 ± 10.8	4.3 ± 0.6	22 ± 25
TCPP	13674-84-5	12.6	277>125 (10)	201>125 (30)	97 ±12	93 ±4.5	118 ± 31	63.1 ± 33.2	4.9 ± 0.8	36 ± 12
TDCP	13674-87-8	17.4	381>159 (10)	209>75 (10)	79 ±1	78 ± 20	81 ± 4	nd	0.5 ± 0.1	4 ± 3
TPhP	115-86-6	18.1	326>169 (30)	215>169 (30)	88 ±18	101 ± 6	88 ± 2	14.3 ± 14.3	10 ± 0.5	13 ± 7
EHDPP	1241-94-7	18.4	251>77 (30)	251>153 (30)	109 ±15	72 ± 38	72 ± 14	2.0 ± 1.9	0.01 ± 0.02	9 ± 7
TEHP	78-42-2	18.6	113>82 (20)	211>99 (20)	82 ±11	111 ± 5	64 ± 11	11.0 ± 7.1	1.3 ± 1	6 ± 11
TCP 1	1330-78-5	20.6	368>197 (20)	368>181 (20)	69 ±34	72 ± 29	99 ± 7	nd	0.07 ± 0.02	11 ± 2
TCP 2	1330-78-5	21.0	368>197 (20)	368>181 (20)	78 ±32	73 ± 20	86 ± 3	nd	0.17 ± 0.06	4 ± 2
TCP 3	1330-78-5	21.3	368>197 (20)	368>181 (20)	96±28	71 ± 22	90 ± 1	nd	nd	3 ± 2
TCP 4	1330-78-5	21.7	368>197 (20)	368>181 (20)	105 ±21	79 ± 29	75 ± 4	nd	nd	2 ± 3

Table S4. OCPs, PCBs and PBDEs studied, CAS number, GC-MS/MS retention time and monitored transitions and collision energies for OCPs and PCBs and by GC-NCI-MS for PBDEs, ordered by retention time. na=not analyzed. Due to the low values, MDL are in ng/g.

COMPOUND	CAS	Rt (min)	Q1(CE, eV)	Q2 (CE, eV)	MDL (ng/g dw) Soil	% R±SD Soil	MDL (ng/g ww) Eggs	% R±SD Eggs
HCBu	87-68-3	9.40	260>225 (10)	260>190 (45)	0.13	76 ± 0.1	0.04	81.4 ± 24
PeCB	608-93-5	15.90	250>215 (30)	250>180 (30)	0.19	80 ± 18	0.07	76 ± 1
α-HCH	319-84-6	19.40	219>147 (20)	219>183 (15)	0.03	97 ± 16	0.11	102 ± 10
HCB	118-74-1	20.55	284>249 (20)	284>114 (20)	0.08	83 ±17	0.04	75 ± 10
β-HCH	319-85-7	20.80	219>147 (20)	219>183 (15)	1.40	115 ± 11	0.18	87 ± 16
γ-HCH	58-89-9	22.10	219>183 (15)	219>147 (20)	0.12	122 ± 9	0.20	92 ± 10
δ-HCH	319-86-8	23.98	219>147 (20)	219>183 (15)	0.13	110 ± 14	0.46	108 ± 4
PCB-28	7012-37-5	24.02	258>186 (30)	258>188 (40)	0.13	77 ± 0.2	1.98	92 ± 11
Heptachlor	76-44-8	24.80	272>237 (20)	272>235 (20)	0.11	78 ±19	0.65	100 ± 6
PCB-52	35693-99-3	26.10	292>222 (45)	292>220 (40)	0.27	82 ± 2	1.04	86 ± 1
Aldrin	309-00-2	26.80	263>193 (40)	263>191 (40)	0.95	88 ± 2	0.44	88 ± 6
DBP	90-98-2	27.60	139>111 (20)	139>75 (30)	na	na	na	na
Isodrin	465-73-6	28.50	263>193 (40)	263>191 (40)	0.55	97 ± 4	1.21	77 ± 5
Heptachlor-epoxide	1024-57-3	29.30	353>191 (45)	353>193 (45)	2.50	105 ± 1	1.07	109 ± 2
Oxychlordane	27304-13-8	29.35	185>121 (20)	185>85 (20)	0.30	97 ± 16	0.14	92 ± 9
cis-Chlordane	5103-71-9	30.70	375>266 (30)	375>339 (20)	0.17	85 ± 9	0.30	86 ± 11
2,4´-DDE	72-55-9	31.30	318>246 (20)	318>248 (20)	0.37	82 ± 1.5	0.62	80 ± 2
α-endosulfan	959-98-8	31.40	195>159 (10)	195>125 (20)	0.02	120 ± 18	0.55	86 ± 3
PCB-101	37680-73-2	31.43	326>256 (50)	326>219 (50)	2.70	79 ± 1	1.70	90 ± 7
transchlordane	5103-74-2	31.65	373>266 (30)	373>264 (30)	0.43	107 ± 17	0.99	87 ± 4
Dieldrin	60-57-1	32.98	241>206 (30)	241>170 (40)	2.60	88 ± 0.5	5.21	85 ± 6
4,4´-DDE	72-55-9	33.25	318>248 (20)	318>246 (20)	0.36	85 ± 10	0.09	76 ± 5
2,4´-DDD	53-19-0	33.70	235>165 (30)	235>200 (20)	0.14	97 ± 11	0.71	115 ± 3

Table S4. (Continued)

COMPOUND	CAS	Rt (min)	Q1(CE, eV)	Q2 (CE, eV)	MDL (ng/g dw) Soil	% R±SD Soil	MDL (ng/g ww) Eggs	% R±SD Eggs
Endrin	72-20-8	34.20	263>193 (20)	263>228 (20)	2.90	100 ± 10	7.71	99 ± 1
β-endosulfan	33213-65-9	34.80	241>206 (15)	241>170 (25)	1.70	102 ± 13	2.04	74 ± 8
2,4´-DDT	789-02-6	35.73	235>165 (40)	235>199 (10)	0.11	112 ± 5	0.74	125 ± 1
4,4´-DDD	72-54-8	35.86	235>165 (40)	235>199 (10)	0.11	89 ± 6	0.74	126 ± 1
PCB-153	35065-27-1	36.53	360>290 (30)	360>288 (30)	0.07	71 ± 1	0.16	108 ± 6
Endosulfan-sulfate	1031-07-8	37.40	272>237 (10)	272>143 (40)	2.90	100 ± 1	5.39	115 ± 10
4,4´-DDT	50-29-3	37.90	235>165 (40)	237>167 (40)	0.38	98 ± 13	1.12	96 ± 15
PCB-138	35065-28-2	38.10	360>290 (40)	360>288 (40)	0.20	109 ± 0.1	3.82	89 ± 13
Dicofol	115-32-2	41.30	139>111 (30)	139>75 (30)	1.00	125 ± 7	1.18	98 ± 9
Methoxychlor	72-43-5	41.53	227>169 (30)	227>115 (50)	0.14	96 ± 26	4.54	110 ± 5
PCB-180	35065-29-3	42.10	394>324 (30)	394>359 (20)	0.04	112 ± 0.3	1.90	106 ± 3
Mirex	2385-85-5	43.06	332>262 (40)	332>260 (50)	0.21	92 ± 2	6.40	106 ± 4
PBDE 28	41318-75-6	9.81	79	161/81	0.43	78 ± 5	2.06	87 ± 1
PBDE 47	5436-43-1	12.34	79	161/81	0.28	71 ± 7	2.06	96 ± 2
PBDE 66	189084-61-5	14.14	79	161/81	0.30	82 ± 4	1.97	101 ± 3
PBDE 100	189084-64-8	14.53	79	161/81	0.05	79 ± 3	1.81	97.2 ± 0.1
PBDE 99	60348-60-9	14.75	79	161/81	0.09	85 ± 6	1.67	103 ± 5
PBDE 85	182346-21-0	15.17	79	161/81	0.45	68 ± 9	1.99	93 ± 1
PBDE 154	207122-15-4	17.95	79	161/81	0.90	89 ± 8	1.53	99 ± 2
PBDE 153	68631-49-2	18.50	79	161/81	0.45	86 ± 7	2.16	86 ± 3
PBDE 138	182677-30-1	20.01	79	161/81	0.22	74 ± 8	1.44	106 ± 3
PBDE 183	207122-16-5	21.18	79	161/81	0.19	95 ± 4	1.43	95 ± 7
PBDE 209	1163-19-5	28.34	486.5	79/81/161	20	105 ± 5	6.36	72 ± 21

Table S5. Predicted no effects concentrations (PNEC) used for risk assessment obtained from NORMAN ecotoxicology database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php).

COMPOUNDS	Lowest PNEC sediment (µg/kg dw)	Lowest PNEC freshwater (µg/L)
TEP	2903	632
TiPP	11.8	0.89
TnPP	22.8	2.32
TnBP	967	76
TCEP	9.27	4
TCPP	120	111
TDCP	20.5	1.1
TPhP	64.4	0.74
EHDPP	2.24	0.018
TEHP	24.3	0.039
TCP 1	11.7	0.023
TCP 2	3.4	0.023
TCP 3	16.3	0.11
TCP 4	7.0	0.023
PBDE 28	646	0.049
PBDE 47	129	0.049
PBDE 66	614	0.019
PBDE 100	1406	0.049
PBDE 99	141	0.049
PBDE 85	259	0.009
PBDE 154	609	0.049
PBDE 153	618	0.049
PBDE 138	68.9	0.0054
PBDE 183	42.8	0.0029
PBDE 209	3553	0.2
PCB 28	239	0.11
PCB 52	139	0.021
PCB 101	82.7	0.01
PCB 153	86	0.0046
PCB 138	145	0.0035
PCB 180	57.4	0.0014
HCBu	50.9	0.6
PeCB	1.1	0.007
α-HCH	1.49	0.02
HCB	13.7	0.05
β-HCH	1.49	0.02
δ-HCH	1.49	0.02
γ-HCH	1.49	0.02
Heptachlor	na	na
Aldrin	24.2	0.01
Isodrin	24.2	0.01
Heptachlor epoxide	0.0001	2.00E-07

Table S5. (Continued)

COMPOUNDS	Lowest PNEC sediment (µg/kg dw)	Lowest PNEC freshwater (µg/L)
Oxychlordane	na	0.013
cis-chlordane	0.15	0.00005
2,4DDE	11.5	0.00076
α-endosulfan	0.0032	0.000005
trans-chlordane	0.15	0.00005
Dieldrin	24.2	0.01
4,4´-DDE	81.6	0.025
2,4´-DDD	14.5	0.0039
Endrin	22.1	0.0051
β-endosulfan	0.0032	0.000005
2,4´-DDT	156	0.025
4,4´-DDD	20.1	0.025
Chlordecone	0.78	0.001
Endosulfan sulphate	62.1	0.95
4,4´-DDT	101	0.01
Dicofol	0.32	0.0013
Metoxychlor	3.06	0.00078
Mirex	2100	0.043

na: not available

Table S6. Concentration of pollutants in hen eggs (µg/g ww) from the Baihe e-waste site. Mean concentrations calculated considering the nd as zeros, not to overestimate concentrations.

COMPOUNDS	**HEN 1**	**HEN 2**	**HEN 3**	**HEN 4**	**HEN 5**	**HEN 6**	**MEAN**
TEP	nd	0.010	0.17	nd	nd	0.014	0.033
TiPP	nd	nd	nd	0.001	nd	nd	0
TnPP	nd	nd	nd	nd	nd	nd	nd
TnBP	nd	nd	0.09	0.093	nd	nd	0.031
TCEP	nd	nd	nd	nd	nd	nd	nd
TCPP	nd	nd	0.09	nd	nd	nd	0.017
TDCP	nd	nd	nd	nd	nd	nd	nd
TPhP	nd	nd	nd	nd	nd	nd	nd
EHDPP	nd	nd	nd	nd	nd	nd	nd
TEHP	nd	nd	nd	0.028	nd	nd	0.006
TCP1	nd	nd	nd	nd	nd	nd	nd
TCP2	nd	nd	nd	nd	nd	nd	nd
TCP3	nd	nd	nd	nd	nd	nd	nd
TCP4	nd	nd	nd	nd	nd	nd	nd
∑OPEs	*nd*	*0.01*	*0.37*	*0.12*	*nd*	*0.01*	*0.086*
PBDE 28	nd	nd	nd	1.48	2.38	nd	0.643
PBDE 47	0.004	0.0006	0.0004	0.001	0.002	0.005	0.002
PBDE 66	nd	nd	nd	0.006	0.014	0.004	0.004
PBDE 100	nd	0.0002	0.0001	0.002	0.003	0.002	0.001
PBDE 99	1.96	0.001	0.0008	0.009	0.022	0.008	0.333
PBDE 85	nd	0.0002	nd	0.006	0.017	0.0006	0.004
PBDE 154	2.88	0.0015	0.002	0.003	0.014	0.014	0.486
PBDE 153	0.08	0.003	0.03	nd	nd	0.08	0.032
PBDE 138	nd	nd	nd	nd	nd	nd	nd
PBDE 183	0.001	0.004	0.005	0.009	0.024	0.27	0.052
PBDE 209	0.05	0.04	0.014	0.033	0.111	0.22	0.078
∑PBDEs	*4.98*	*0.05*	*0.05*	*1.55*	*2.59*	*0.60*	*1.636*
PCB 28	0.006	0.017	0.018	0.008	0.008	0.34	0.066
PCB 52	nd	nd	0.002	0.002	0.34	0.007	0.059
PCB 101	0.002	0.03	0.014	0.0004	0.002	0.087	0.023
PCB 153	0.004	0.099	0.047	0.004	0.013	0.38	0.091
PCB 138	0.008	0.125	0.06	nd	0.018	0.51	0.120
PCB 180	0.002	0.022	0.012	nd	0.002	0.071	0.018
∑PCBs	*0.02*	*0.29*	*0.15*	*0.01*	*0.38*	*1.40*	*0.377*
HCBu	0.002	0.001	0.001	0.001	0.001	0.001	0.001
PeCB	0.002	0.002	0.002	0.002	0.002	0.002	0.002
α-HCH	0.001	0.001	0.001	0.0003	0.0005	0.0005	0.001
HCB	0.0006	0.001	0.002	0.001	0.001	0.002	0.001
β-HCH	nd	0.001	0.001	nd	0.0002	0.0001	0.0004
δ-HCH	0.0002	0.0003	0.400	0.0003	0.0001	0.0004	0.067
γ-HCH	nd	nd	nd	nd	nd	nd	nd
α-endosulfan	nd	nd	nd	nd	nd	nd	nd
trans-chlordane	0.0001	0.010	0.005	nd	0.0004	0.001	0.003

Table S6. (Continued)

COMPOUNDS	HEN 1	HEN 2	HEN 3	HEN 4	HEN 5	HEN 6	MEAN
4,4-DDE	nd	nd	nd	nd	nd	nd	nd
β-endosulfan	nd	nd	nd	nd	nd	nd	nd
4,4-DDD	nd	0.001	0.0004	nd	nd	0.0001	0.0003
Chlordecone	0.0004	0.0001	0.0004	0.0006	0.0007	0.0002	0.0004
4,4-DDT	nd	0.007	0.002	nd	nd	0.0004	0.002
Metoxychlor	nd	nd	nd	nd	nd	nd	nd
Mirex	nd	nd	0.003	nd	nd	0.035	0.019
∑OCPs	*0.01*	*0.02*	*0.42*	*0.01*	*0.01*	*0.04*	*0.084*
∑Pollutants	*5*	*0.4*	*1.0*	*1.7*	*3.0*	*2.1*	*2.18*