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Supporting Information

Organophosphate flame retardants and diesters in urine of e-waste dismantling workers: Associations with indoor dust and implications for urinary biomonitoring

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Reagents and materials

Strata-X-AW cartridge (60 mg/3 mL) was purchased from Phenomenex Inc. (Torrance, USA), while Florisil cartridge (500 mg/6 mL) was purchased from Anpu experimental technology (Shanghai, China). Acetone (ACE), methyl tert-butyl ether (MTBE), n-hexane (HEX), dichloromethane (DCM), ethyl acetate, and acetonitrile are all chromatography grade and purchased from Anpu experimental technology (Shanghai, China). Methanol (chromatography grade, MEOH) was bought from Darmstadt, Germany. Ultra-pure water was obtained from a Milli-Q system (Millipore, Gananda), β-glucuronidase and sulfatase were bought from Sigma-Aldrich (St. Louis, MO). The LC column Poroshell 120 EC-C18 and Kinetex EVO-C18 100A were purchased from Agilent (Santa Clara, CA, USA) and Phenomenex (Torrance, CA, USA), respectively.

27 **Table S1** Targeted analytes investigated in the present study

Analytes	Abbreviation	Formula	CAS number	Internal standards
PFRs				
triphenyl phosphate	TPHP	$C_{18}H_{15}O_4P$	115-86-6	d_{15}-TPHP
tributyl phosphate	TNBP	$C_{12}H_{27}O_4P$	126-73-8	d_{27}-TNBP
tris(2-butoxyethyl) phosphate	TBOEP	$C_{18}H_{39}O_7P$	78-51-3	d_{27}-TNBP
tris(2-Chloroethyl) phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	115-96-8	d_{12}-TCEP
tris(1-chloro-2-propyl) phosphate	TCIPP	$C_9H_{18}Cl_3O_4P$	13674-84-5	d_{18}-TCIPP
tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	$C_9H_{15}Cl_6O_4P$	13674-87-8	d_{15}-TDCIPP
tris-(2-ethylhexyl) phosphate	TEHP	$C_{24}H_{51}O_4P$	78-42-2	d_{27}-TNBP
2-ethylhexyl diphenyl phosphate	EHDPHP	$C_{20}H_{27}O_4P$	1241-94-7	d_{27}-TNBP
DAPs				
diphenyl phosphate	DPHP	$C_{12}H_{11}O_4P$	838-85-7	d_{10}-DPHP
dibutyl phosphate	DBP	$C_{18}H_{19}O_4P$	107-66-4	d_{18}-DBP
bis(butoxyethyl) phosphate	BBOEP	$C_{12}H_{27}O_6P$	14260-97-0	d_8-BBOEP
bis(2-chloroethyl) phosphate	BCEP	$C_4H_9Cl_2O_4P$	3040-56-0	d_8-BCEP
bis(1-chloro-2-propyl) phosphate	BCIPP	$C_6H_{13}Cl_2O_4P$	789440-10-4	d_{12}-BCIPP
bis(1,3-dichloro-2-propyl) phosphate	BDCIPP	$C_6H_{11}Cl_4O_4P$	72236-72-7	d_{10}-BDCIPP

29 **Table S2** General information for the thirty volunteers

Subject Number	Gender	Age (year)	Occupational exposure time (year)	BMI (kg/m^2)	Wash hands more than 5 times per day	Use detergent
1	Male	42	12	28.3	Yes	Yes
2	Female	43	12	27.3	Yes	Yes
3	Male	72	8	22.3	Yes	Yes
4	Male	40	6.5	22.5	Yes	Yes
5	Male	39	8	24.6	Yes	Yes
6	Female	33	8	18.5	Yes	Yes
7	Female	36	9	21.9	No	Yes
8	Male	40	10	20.2	Yes	No
9	Female	35	10	18.0	Yes	No
10	Female	40	10	21.2	Yes	Yes
11	Male	42	10	19.7	Yes	Yes
12	Female	44	14	24.2	Yes	Yes
13	Male	41	14	26.6	Yes	Yes
14	Female	39	16	21.8	No	No
15	Male	36	8	20.6	Yes	No
16	Female	35	10	19.5	Yes	No
17	Male	38	10	21.3	Yes	No
18	Male	50	11	25.6	Yes	Yes
19	Female	42	11	18.8	No	Yes
20	Female	46	13	20.3	Yes	Yes
21	Male	48	13	27.0	Yes	Yes
22	Male	18	13	22.0	Yes	Yes
23	Male	50	20	27.7	Yes	Yes
24	Female	45	20	22. 9	Yes	Yes
25	Female	50	12	23.4	Yes	Yes
26	Male	53	12	20.6	Yes	Yes
27	Male	59	15	19.5	Yes	Yes
28	Female	53	15	23.4	No	Yes
29	Male	43	12	23.2	No	No
30	Female	37	12	19.6	No	No

31 **Table S3** MS/MS parameters for targeted analytes

Analytes	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (V)	Collision energy (V)
Positive polarity					
TPHP	11.4	327	77.0/152	114/102	59.4/49.4
TNBP	11.9	267	99.0/155	64.5/65.0	21.1/14.9
TBOEP	12.2	399	299/199	76.7/80.0	18.3/21.1
TCEP	6.84	287	99.0/63.1	68.2/68.7	34.8/41.1
TCIPP	10.0	327	99.0	64.6	29.8
TDCIPP	11.3	431	99.0	81.8	42.0
TEHP	15.5	435	99.0/71.0	81.2/78.6	23.4/32.6
EHDPHP	13.1	363	251	71.8	10.6
Negative polarity					
DPHP	1.82	250	93.9/155	78.2/72.7	30.9/29.0
DBP	2.50	209	79.0/153	67.1/62.8	24.4/18.8
BBOEP	4.42	298	79.1/197	98.8/89.8	30.9/24.0
BCEP	0.92	221	35.1	33.0	18.8
BCIPP	1.44	249	35.2	29.1	18.9
BDCIPP	3.06	319	35.0/37.1	42.9/47.8	24.0/18.9

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34 **Table S4** Levels of target chemicals detected in procedural blanks for dust sample analysis (ng/g)

Analytes	Blank-1	Blank-2	Blank-3	Blank-4	Blank-5	Blank-6
PFRs						
TPHP	nd	nd	nd	nd	nd	nd
TNBP	nd	nd	nd	nd	nd	nd
TBOEP	nd	0.17	0.09	nd	nd	nd
TCEP	nd	nd	nd	nd	nd	nd
TCIPP	nd	nd	nd	nd	nd	nd
TDCIPP	nd	nd	nd	nd	nd	nd
TEHP	nd	nd	nd	nd	nd	nd
EHDPHP	nd	nd	nd	nd	nd	nd
DAPs						
DPHP	nd	nd	nd	nd	nd	nd
DBP	nd	nd	nd	nd	nd	nd
BBOEP	nd	nd	nd	nd	nd	nd
BCEP	0.42	0.45	0.75	0.11	0.56	0.43
BCIPP	nd	nd	nd	nd	nd	nd
BDCIPP	nd	nd	nd	nd	nd	nd

35 nd, not detected

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Table S5 Levels of target chemicals detected in procedural blanks for urine sample analysis (ng/mL)

Analytes	Blank-1	Blank-2	Blank-3	Blank-4	Blank-5	Blank-6
PFRs						
TPHP	nd	nd	nd	nd	nd	nd
TNBP	nd	nd	nd	nd	nd	nd
TBOEP	nd	nd	nd	nd	nd	nd
TCEP	nd	nd	nd	nd	nd	nd
TCIPP	nd	nd	nd	nd	nd	nd
TDCIPP	nd	nd	nd	nd	nd	nd
TEHP	nd	nd	nd	nd	nd	nd
EHDPHP	nd	nd	nd	nd	nd	nd
DAPs						
DPHP	nd	nd	nd	nd	nd	nd
DBP	nd	nd	nd	nd	nd	nd
BBOEP	nd	nd	nd	nd	nd	nd
BCEP	nd	nd	nd	nd	nd	nd
BCIPP	nd	nd	nd	nd	nd	nd
BDCIPP	nd	nd	nd	nd	nd	nd

nd, not detected

Table S6 Recoveries of target chemicals in spiked dust samples (%)

Analytes	Spiked Matrix (n = 3)		Spiked Blank (n = 3)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
PFRs				
TPHP	92	8.4	106	5.5
TNBP	109	6.5	101	1.8
TBOEP	128	7.0	117	12
TCEP	95	7.0	99	1.7
TCIPP	101	9.5	111	3.7
TDCIPP	105	6.9	106	2.2
TEHP	94	6.7	86	8.9
EHDPHP	86	10	94	11
DAPs				
DPHP	116	12	109	5.6
DBP	119	11	112	10
BBOEP	115	7.8	104	8.8
BCEP	104	9.1	113	12
BCIPP	93	13	103	11
BDCIPP	112	4.2	107	4.8

Table S7 Recoveries of target chemicals in spiked urine samples (%)

Analytes	Spiked Matrix (n = 3)		Spiked Blank (n = 3)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
PFRs				
TPHP	98	1.1	107	1.0
TNBP	92	1.0	8 8	2.4
TBOEP	87	4.4	93	5.2
TCEP	104	3.8	94	2. 8
TCIPP	101	1.0	94	0.3
TDCIPP	103	0.6	96	4.6
TEHP	89	7.1	103	1.0
EHDPHP	96	8.5	97	11
DAPs				
DPHP	93	2.2	101	11
DBP	102	4.3	107	3.0
BBOEP	101	6.1	105	4.5
BCEP	97	9.7	114	6.3
BCIPP	120	9.6	108	5.7
BDCIPP	112	4.2	102	7.6

Table S8 Correlation matrix for log-transformed PFR levels measured in dust samples

	TPHP	TBOEP	TEHP	EHDPHP	TCEP	TCIPP	TDCIPP	DPHP	BCEP
TPHP	1.000	0.330	**0.546****	0.269	**0.434***	0.229	0.307	**0.949****	-0.277
TBOEP		1.000	**0.660****	**0.627****	**0.631****	0.132	**0.597****	0.312	0.256
TEHP			1.000	**0.734****	**0.595****	-0.048	**0.556****	**0.583****	0.168
EHDPHP				1.000	**0.516****	0.119	**0.558****	0.297	0.254
TCEP					1.000	-0.025	**0.656****	**0.443***	0.209
TCIPP						1.000	0.029	0.299	-0.155
TDCIPP							1.000	0.277	0.168
DPHP								1.000	-0.208
BCEP									1.000

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

Table S9 Correlation matrix for log-transformed DAP levels measured in urine samples

	Morning urine				Nightfall urine			
	DPHP	**BDCIPP**	**BCEP**	**TCIPP**	**DPHP**	**BDCIPP**	**BCEP**	**TCIPP**
DPHP	1.000				1.000			
BDCIPP	**0.379****	1.000			**0.481****	1.000		
BCEP	0.242	-0.058	1.000		0.373	0.207	1.000	
TCIPP	-0.238	0.137	0.082	1.000	-0.143	-0121	0.201	1.00
Age	**0.419***	-0.137	-0.026	0.045	**0.398***	-0.217	0.106	0.064
Exposure time	0.198	-0.196	**0.416****	0.203	-0.054	-0.252	**0.523***	0.400

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

Table S10 Concentrations of PFRs measured in individual urine samples (ng/mL)

NO.	Morning Urine						Enveing Urine					
	TPHP	**TNBP**	**TCEP**	**TCIPP**	**TDCIPP**	**ΣPFRs**	**TPHP**	**TNBP**	**TCEP**	**TCIPP**	**TDCIPP**	**ΣPFRs**
1	nd	nd	nd	0.10	nd	0.10	nd	nd	nd	nd	0.05	0.05
2	0.03	nd	nd	0.25	0.07	0.35	nd	nd	nd	nd	nd	nd
3	nd	nd	nd	0.08	nd	0.08	nd	0.24	nd	0.09	0.03	0.36
4	nd	nd	nd	0.06	0.04	0.10	0.03	nd	nd	nd	nd	0.03
5	nd	0.32	0.86	0.10	0.13	1.41	0.02	2.82	0.77	0.25	0.06	3.92
6	nd	nd	nd	nd	0.07	0.07	nd	2.10	1.08	0.14	0.05	3.37
7	nd	nd	nd	0.10	nd	0.10	nd	0.16	nd	0.06	0.14	0.36
8	nd	nd	nd	nd	nd	nd	nd	0.16	nd	nd	nd	0.16
9	nd	nd	nd	0.12	0.04	0.16	nd	0.16	0.21	0.07	nd	0.43
10	nd	nd	nd	0.07	nd	0.07	nd	5.19	nd	0.08	nd	5.27
11	nd	0.55	nd	0.05	0.09	0.69	nd	2.50	nd	nd	0.32	2.82
12	nd	nd	nd	nd	nd	nd	nd	0.35	nd	0.09	0.08	0.51
13	nd	0.39	0.72	0.13	0.09	1.34	nd	4.67	0.13	nd	0.06	4.86
14	0.14	0.26	nd	0.36	0.12	0.87	0.02	nd	0.11	0.09	nd	0.23
15	nd	nd	nd	nd	nd	nd	0.04	nd	0.12	0.07	0.04	0.27
16	nd	nd	nd	0.05	nd	0.05	nd	nd	0.12	0.05	nd	0.17
17	nd	nd	nd	nd	0.04	0.04	nd	nd	nd	nd	nd	nd
18	nd	0.42	nd	nd	0.04	0.46	nd	0.31	nd	0.10	nd	0.41
19	nd	0.69	nd	0.05	nd	0.75	0.02	1.18	0.16	0.08	0.14	1.59
20	nd	0.26	nd	0.14	1.36	1.76	nd	2.51	0.10	0.13	nd	2.74
21	0.24	0.21	nd	nd	nd	0.45	nd	0.46	nd	0.06	nd	0.52
22	nd	0.20	nd	0.18	0.24	0.62	nd	nd	nd	nd	0.04	0.04
23	nd	0.73	0.13	0.25	0.06	1.16	nd	nd	0.14	0.12	nd	0.26
24	0.16	nd	nd	0.24	nd	0.40	0.37	0.14	0.10	0.40	0.07	1.08
25	nd	0.33	0.31	0.22	0.08	0.94	nd	nd	nd	0.06	nd	0.06
26	nd	nd	nd	nd	0.14	0.14	nd	0.21	0.18	0.06	0.07	0.52
27	nd	nd	nd	nd	nd	nd	0.03	0.47	0.18	0.10	nd	0.78
28	nd	nd	nd	0.07	0.09	0.16	nd	nd	nd	nd	nd	nd
29	0.02	0.11	nd	0.12	nd	0.25	nd	nd	0.25	nd	nd	0.25
30	nd	nd	nd	0.09	nd	0.09	0.04	0.19	0.36	0.10	nd	0.69

nd, not detected

Table S11 Concentrations of DAPs measured in individual urine samples (ng/mL)

NO.	Morning Urine							Enveing Urine						
	DPHP	BDCIPP	DBP	BBOEP	BCIPP	BCEP	ΣDAPs	DPHP	BDCIPP	DBP	BBOEP	BCIPP	BCEP	ΣDAPs
1	nd	0.51	0.17	nd	nd	0.68	1.35	0.56	0.80	0.14	nd	nd	8.66	10.2
2	0.48	0.37	0.15	nd	nd	4.16	5.15	1.73	0.38	0.11	nd	nd	19.5	21.7
3	0.66	0.62	0.25	nd	nd	2.26	3.79	0.92	0.55	0.12	nd	nd	1.76	3.36
4	nd	0.63	nd	nd	nd	nd	0.63	1.75	2.39	0.18	nd	0.28	2.97	7.56
5	0.32	0.67	0.12	nd	nd	nd	1.12	0.46	0.57	0.25	nd	nd	7.69	8.96
6	0.28	0.48	0.19	nd	nd	nd	0.95	0.37	0.47	0.18	nd	nd	nd	1.02
7	nd	nd	nd	nd	nd	nd	nd	0.29	0.44	nd	nd	nd	0.73	1.47
8	0.77	0.64	0.18	nd	nd	nd	1.58	0.57	0.30	nd	nd	nd	5.36	6.23
9	nd	0.34	nd	nd	nd	2.27	2.61	0.51	3.35	0.16	nd	nd	7.65	11. 7
10	nd	nd	nd	nd	nd	nd	nd	0.22	0.28	nd	nd	nd	nd	0.51
11	0.30	0.88	0.18	nd	nd	nd	1.36	0.66	0.44	0.12	nd	nd	6.81	8.02
12	0.34	nd	nd	nd	nd	3.92	4.26	0.35	0.35	nd	nd	nd	0.21	0.91
13	nd	nd	0.11	nd	nd	1.49	1.60	nd	nd	nd	nd	nd	nd	nd
14	0.34	nd	0.20	nd	nd	0.32	0.85	0.29	0.41	nd	nd	nd	0.25	0.94
15	0.28	18.5	0.36	nd	0.61	nd	19.8	0.26	20.4	0.10	nd	0.70	9.62	31.1
16	0.54	0.54	0.16	nd	nd	nd	1.24	0.70	0.39	nd	nd	nd	nd	1.09
17	0.58	1.32	nd	nd	0.34	1.89	4.13	0.37	0.73	0.10	nd	nd	12.1	13.3
18	0.30	0.72	nd	nd	nd	nd	1.03	1.06	0.60	nd	nd	nd	8.71	10.4
19	nd	nd	nd	nd	nd	3.09	3.09	0.84	0.53	0.15	nd	0.27	16.8	18.2
20	0.24	0.66	2.25	nd	nd	3.82	6.98	0.20	0.29	nd	nd	nd	7.52	8.01
21	0.66	0.41	0.17	nd	0.26	6.97	8.47	0.20	nd	nd	nd	nd	nd	0.20
22	0.61	1.13	0.22	nd	nd	1.63	3.58	1.94	0.54	nd	nd	nd	40.5	43.0
23	0.23	0.92	0.28	nd	nd	0.45	1.88	0.40	0.87	nd	nd	0.52	41.8	43.6
24	0.69	1.90	0.46	nd	0.67	20.6	24.4	0.62	1.13	0.11	nd	0.53	32.8	35.2
25	0.86	0.96	0.36	nd	0.58	11.7	14.5	1.66	0.55	0.11	nd	1.41	nd	3.72
26	2.03	1.04	0.12	nd	0.58	nd	3.77	3.98	0.60	nd	nd	1.36	nd	5.94
27	2.73	0.44	nd	nd	1.07	16.5	20.7	1.07	0.36	nd	nd	0.41	8.40	10.3
28	3.28	0.81	0.45	nd	4.13	9.43	18.1	0.52	0.26	nd	nd	0.46	2.30	3.54
29	0.17	0.35	nd	nd	nd	9.61	10.1	0.37	0.64	nd	nd	nd	9.47	10.5
30	0.26	0.50	nd	nd	nd	nd	0.76	0.29	0.58	nd	nd	nd	4.16	5.03

nd, not detected

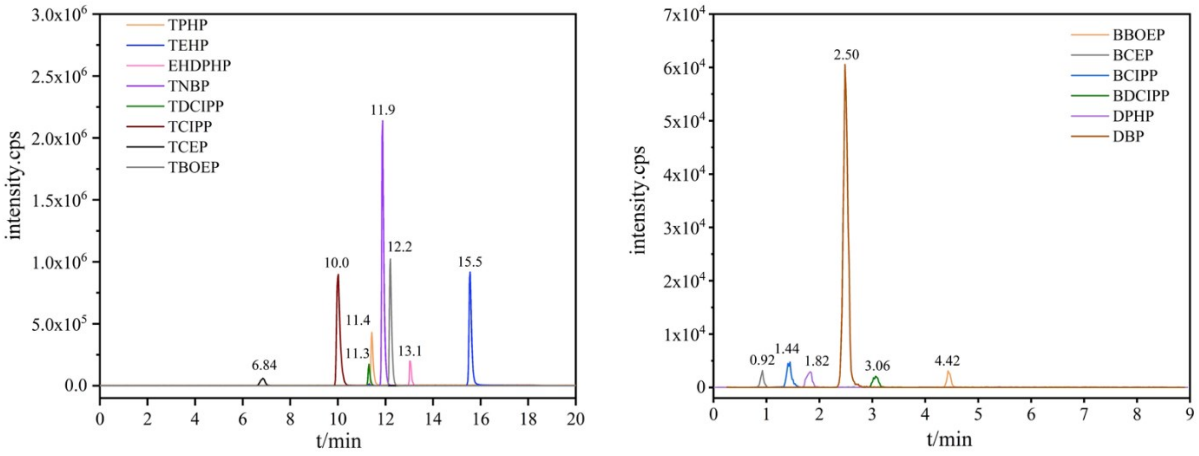

Fig. S1 Chromatograms of PFRs (Left) and DAPs (Right) in LC-MS/MS

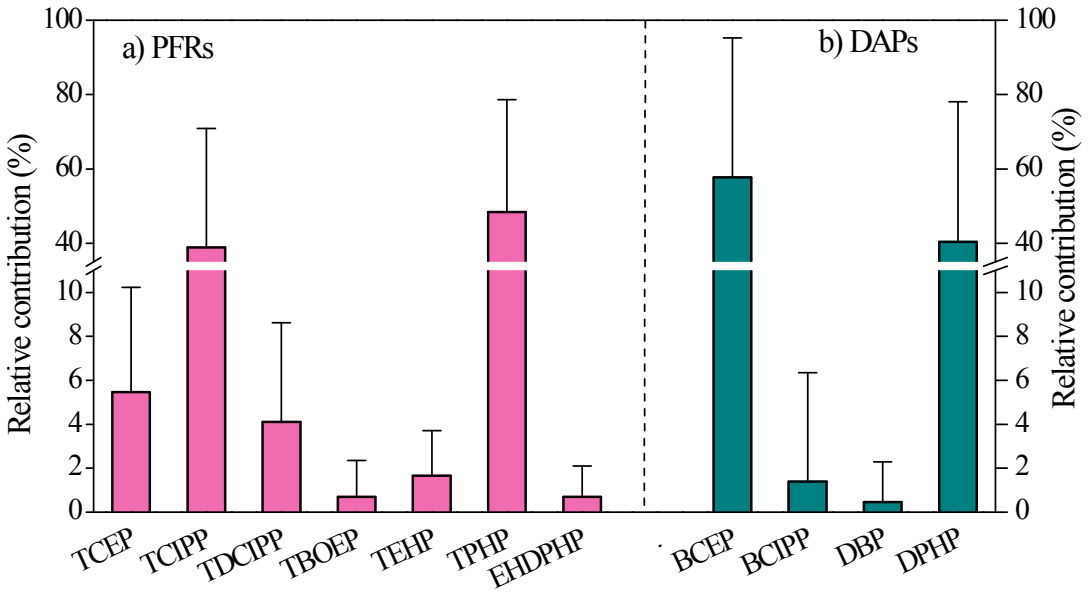

Fig. S2 Relative contributions of individual PFRs (a) and DAPs (b) in indoor dust samples.

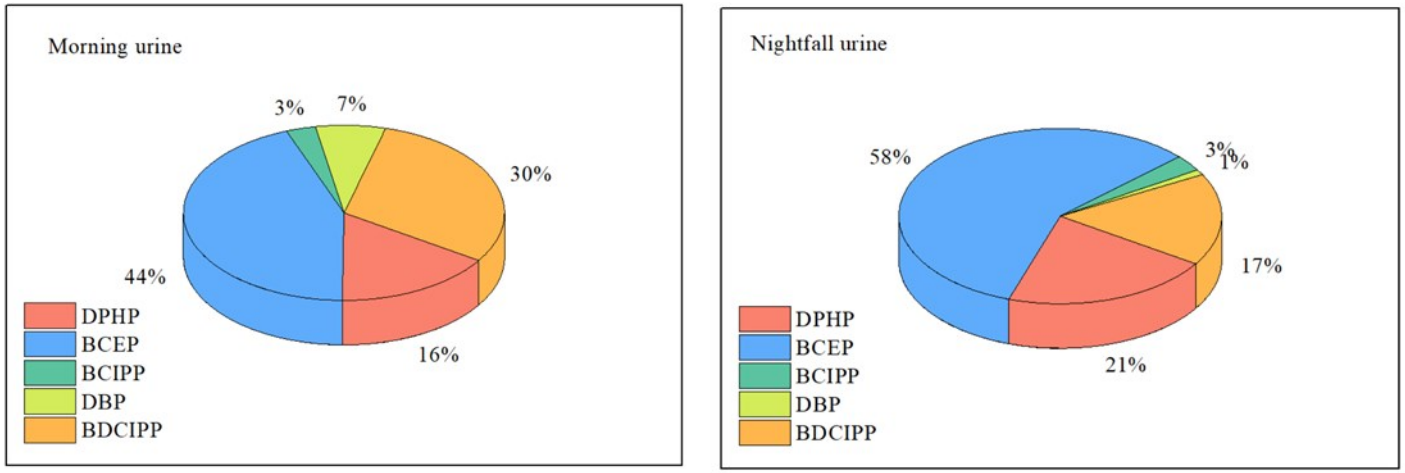

Fig. S3 Composition profiles of DAPs in urine samples of e-waste dismantling workers