Supporting Information

Effect of E-waste Recycling on Urinary Metabolites of Organophosphate Flame Retardants and Plasticizers and Their Association with Oxidative Stress

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Supporting information including description of reagents and solvents, standard preparation; and 2 tables (Table S1-S2) and 3 figures (Figure S1-S4).

Materials and Methods

Standard Preparation. Stock solutions of individual mOP and corresponding labeled standards were prepared in methanol. Calculated volumes of stock solutions were added to a 5 mL volumetric flask to make a mixture of the native standards (NSM), which included BBOEP and DPHP at 400 ng/mL, BDCIPP, BCIPP, BCEP, DBP, DoCP and DpCP at 200 ng/mL. Similarly, the mixture of the internal standards (ISM) was prepared in methanol, which included d_8-BBOEP, d_{10}-DPHP, d_{10}-BDCIPP, d_{12}-BCIPP, d_8-BCEP, d_{18}-DBP, d_{14}-DoCP and d_{14}-DpCP at the same concentration of 200 ng/mL. All standards were stored at -20°C in the laboratory.

Literature Cited

(1) Lu, S. Y.; Li, Y. X.; Zhang, J. Q.; Zhang, T.; Liu, G. H.; Huang, M. Z.; Li, X.; Ruan, J. J.; Kannan, K.; Qiu, R. L. Associations between polycyclic aromatic hydrocarbon (PAH) exposure and oxidative stress in people living near e-waste recycling facilities in China. *Environ. Int.* **2016**, *94*, 161–169.

(2) Zhang, T.; Xue, J.; Gao, C.; Qiu, R.; Li, Y.; Li, X.; Huang, M.; Kannan, K. Urinary concentrations of bisphenols and their association with biomarkers of oxidative stress in people living near e-waste recycling facilities in China. *Environ. Sci. Technol.* **2016**, *50*, 465 4045–4053.

Table S1. Optimized MS/MS Parameters for Target Organophosphate Metabolites [a].

analytes (i.e., metabolites)	parent compounds	precursor ion (Q1)	product ion (Q3)	DP (V)	EP (V)	CE (V)	CXP (V)
native standards							
bis(2-chloroethyl) phosphate (BCEP)	tris(2-chloroethyl) phosphate (TCEP)	221.0	35.0	-60	-7	-30	-16
bis(1-chloro-2-propyl) phosphate (BCIPP)	tris(1-chloro-2-propyl) phosphate (TCIPP)	249.0	35.0	-50	-7	-40	-17
bis(1,3-dichloro-2-propyl) phosphate (BDCIPP)	tris(1,3-dichloro-2-propyl) phosphate (TDCIPP)	318.9	35.0	-53	-4.5	-46	-11
bis(2-butoxyethyl) phosphate (BBOEP)	tris(2-butoxyethyl) phosphate (TBOEP)	305.0	79.0	-70	-8	-40	-15
dibutyl phosphate (DBP)	tri-*n*-butyl phosphate (TNBP)	209.2	78.9	-80	-7	-30	-15
di-o-cresyl phosphate (DoCP)	tricresyl phosphate (TCP)	227.1	107.0	-80	-6	-33	-17
di-p-cresyl phosphate (DpCP)	tricresyl phosphate (TCP)	227.1	107.0	-80	-8	-32	-15
diphenyl phosphate (DPHP)	triphenyl phosphate (TPHP)/ethylhexyl diphenyl phosphate (EHDPP)	249.1	93.0	-100	-7	-45	-9
internal standards							
d_8-BCEP	none	229.0	35.1	-50	-5	-35	-16
d_{12}-BCIPP	none	261.1	35.0	-60	-8	-40	-13
d_{10}-BDCIPP	none	329.0	35.0	-90	-10	-60	-17
d_8-BBOEP	none	305.0	79.0	-90	-7	-60	-10
d_{18}-DBP	none	227.3	79.0	-80	-8	-50	-10
d_{14}-DoCP	none	291.1	114.0	-90	-7	-40	-10
d_{14}-DpCP	none	291.1	114.0	-120	-7	-36	-10
d_{10}-DPHP	none	259.2	98.0	-90	-8	-32	-12

[a] DP = declustering potential; EP = entrance potential; CE = collision energies; CXP = collision cell exit potential.

Table S2. Detailed Information of Subjects Recruited in This Study.

sampling sites	total	age distribution				gender distribution	
		0 > - 6 yrs	> 6 - 18 yrs	> 18 - 60 yrs	> 60 yrs	males	females
e-waste dismantling area	**175**	25	38	88	24	96	79
rural reference area	**29**	4	4	15	6	16	13
urban reference area	**17**	0	0	17	0	9	8

Table S3. Geometric Mean Urinary Concentrations (ng/mL) of Organophosphate Metabolites in 18-60 Age Group Participants Living E-waste Dismantling and Reference Areas in China

	BCEP	**BCIPP**	**BDCIPP**	**BBOEP**	**DBP**	**DoCP&DpCP**	**DPHP**
e-waste dismantling area	0.76	0.089	0.075	0.069	0.12	0.013	0.53
rural control area	0.44	0.081	0.076	0.059	0.10	0.010	0.41
urban control area	0.43	0.028	0.019	0.093	0.10	0.012	0.67

Table S4. Associations between Urinary 8-OHdG Levels and Sum Urinary Concentrations of Cl–mOPs, NCl–mOPs, OH-PAHs, and BPs in Participants Living in E-waste Dismantling Area, Estimated by Linear Regression Analysis. [a]

	β	**standard coefficients**	***p***
∑Cl-mOPs	0.002	0.005	0.958
∑NCl-mOPs	0.234	0.231	0.028
∑OH-PAHs	-0.072	-0.148	0.144
∑BPs	0.119	0.189	0.078

[a]Cl-mOPs and NCl-mOPs are chlorinated and nonchlorinated organophosphate metabolites, respectively, OH-PAHs and BPs are monohydroxy-polycyclic aromatic hydrocarbons and bisphenols, respectively; ∑Cl-mOPs represent the sum urinary concentrations of BCEP, BCIPP and BDCIPP, ∑NCl-mOPs represent the sum urinary levels of BBOEP, DBP, DoCP&DpCP, and DPHP, ∑OH-PAHs represent the sum urinary concentrations of 10 OH-PAHs which previously published by our group,[1] ∑OH-BPs represent the sum urinary levels of BPA and 7 its analogues which previously published by our group;[2] all chemicals were analyzed in the same set of urine samples; log-transformed concentrations were used for analysis.

Figure S1. Sampling locations of urine samples collected from e-waste dismantling and two reference areas in Guangdong Province, China. Yellow background represents Qingyuan City.

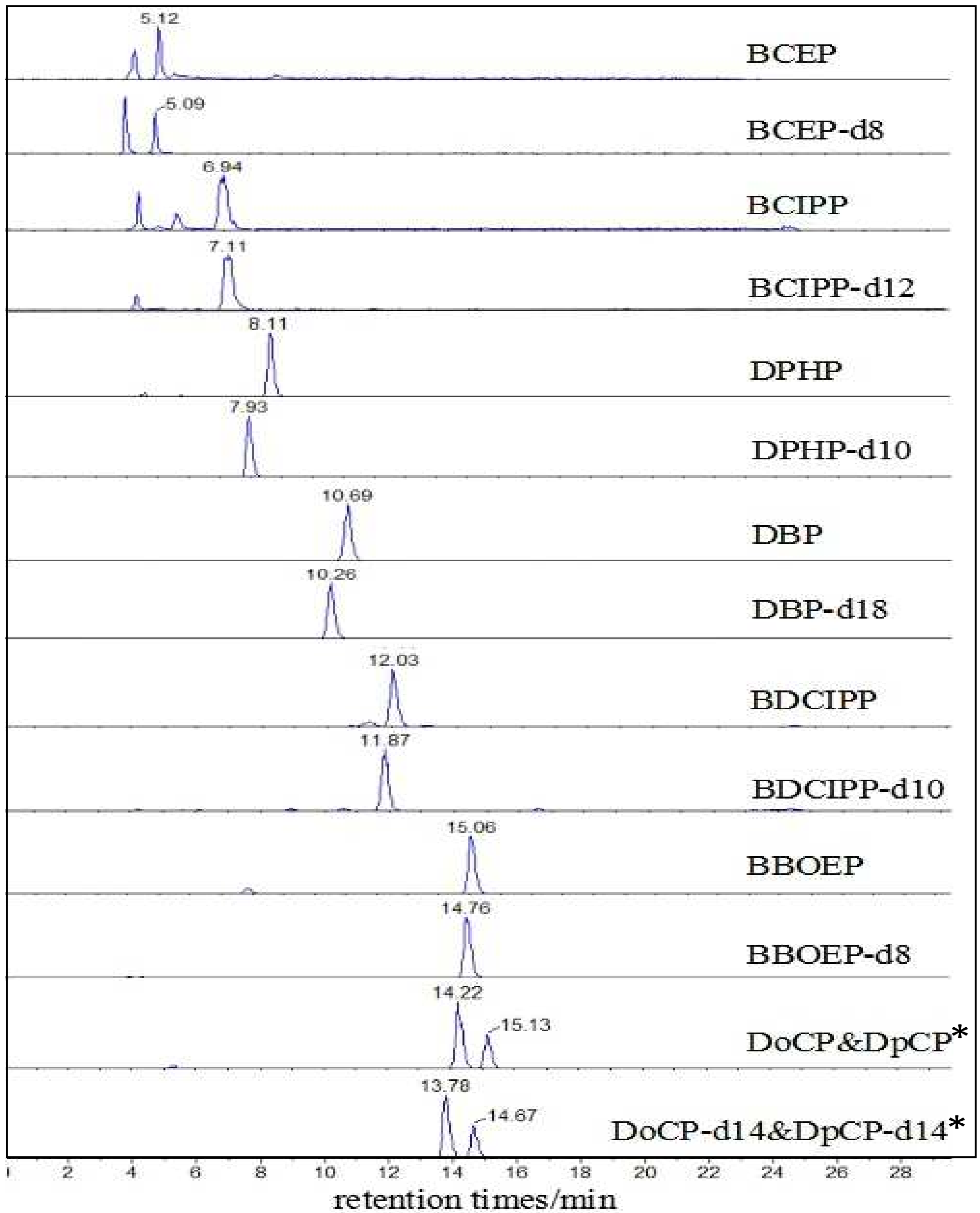

Figure S2. Typical HPLC-MS/MS chromatogram of an extract of a 2 mL urine sample spiked with a 10 ng/mL internal standard mixture of eight mOPs. * The retention time of DoCP and DpCP were 14.22 amd 15.13 mins, respectively; and the retention time of DoCP-d14 and DpCP-d14 were 13.78 amd 14.67 mins. Although there were two peaks shown in this figure for DoCP and DpCP, both of chemicals could not be completely separated from each other in most of samples due to low concentrations; furthermore, DoCP and DpCP were metabolites of the same OP [i.e., tricresyl phosphate (TCP)]; therefore, both of chemicals were referred to as DoCP&DpCP.

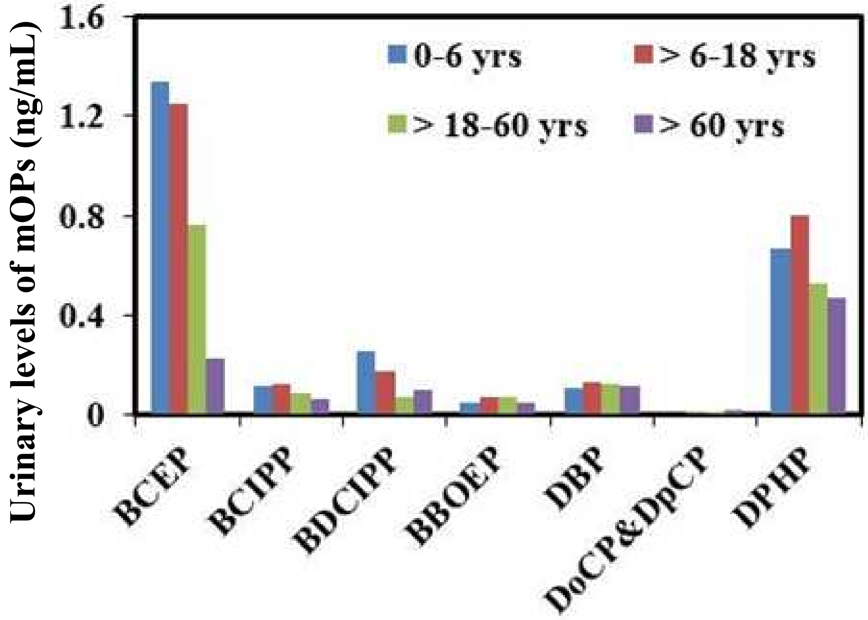

Figure S3. Geometric mean urinary mOPs levels for participants from various age groups living in e-waste dismantling sites of China.

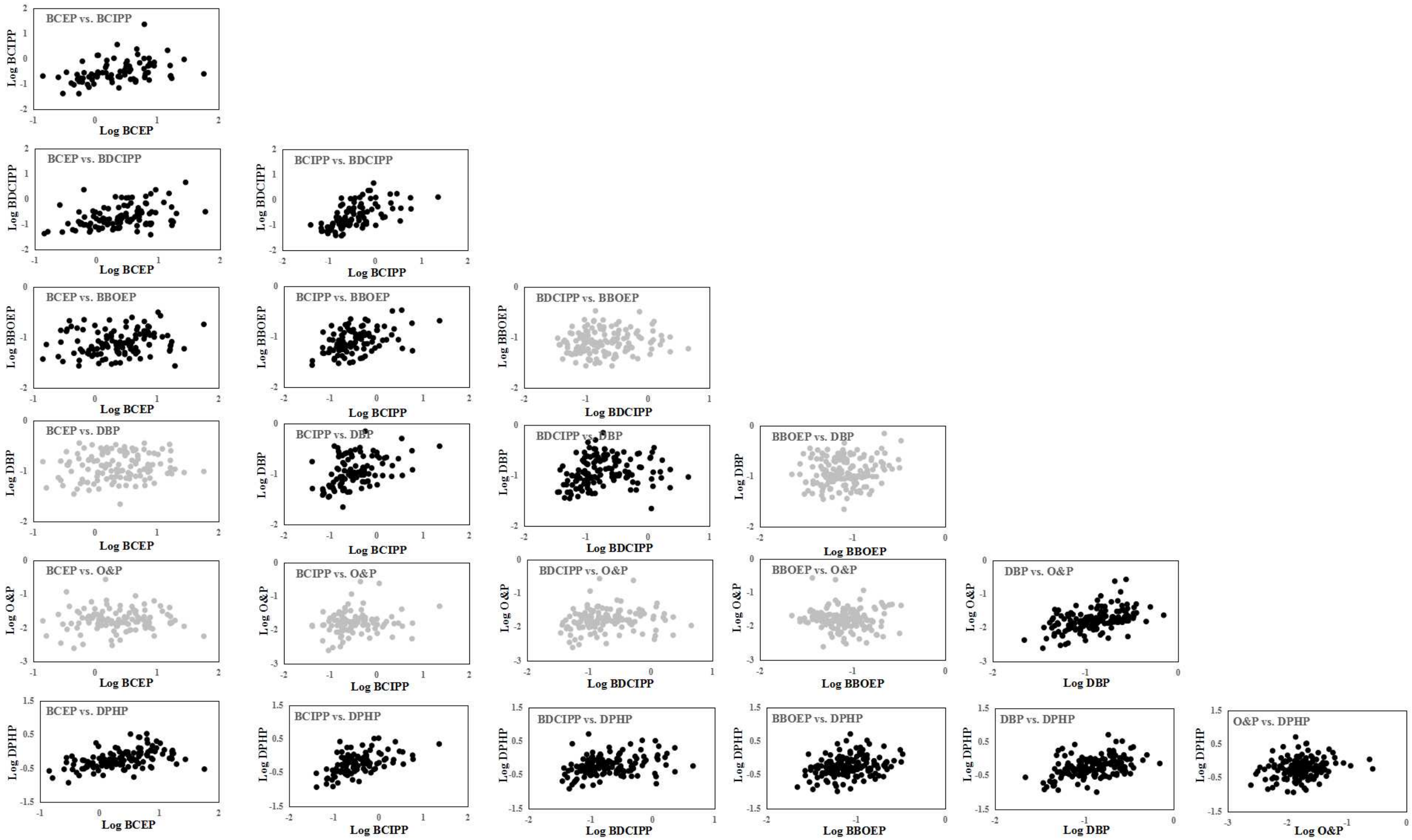

Figure S4. Pearson correlations among individual organophosphate metabolites in urine samples collected in southern China. Concentration values less than LOQ were excluded from these association analyses, and we used log-transformed urinary concentrations for these analyses. The black points represented significant correlations, grey points represented non-significant associations. O&P = DoCP&DpCP.