Supporting Information for

Uptake and Metabolism of Phthalate Esters by Edible Plants

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One figure (Figure S1), seven tables (Table S1-S7), 13 pages.

Content

Supplemental Materials and Methods

Instrumental analysis on GC-MS 3

Instrumental analysis on UPLC-MS/MS 4

Supplemental Tables and Figures

Table S1. 5

Table S2. 6

Table S3. 7

Table S4. 8

Table S5. 9

Table S6. 10

Table S7. 11

Figure S1. 12

References 13

GC-MS Instrumental analysis for PAEs

In this study, concentrations of PAEs were quantified using an Agilent 6890GC-5973 MSD gas chromatograph-mass spectrometer and a 30 m × 0.25 mm × 0.25 μm DB-5MS capillary column (J&W Scientific, Folsom, CA). Samples (1.0 μL) were injected in splitless mode with an inlet temperature of 300 °C. The initial oven temperature was 80 °C for 1.0 min, ramped at 10 °C/min to 180 °C (hold 1 min), then at 2 °C/min to 260 °C (hold 1 min), and finally ramped at 10 °C/min to 300 °C (hold 5 min). Helium (purity > 99.999%) gas was used as a carrier with a constant flow rate of 0.8 mL min^{-1}. The mass selective detector was operated in in electron impact (EI) and selective ion monitoring (SIM) mode. The temperatures of the ion source, quadrupole and transfer line were 230 °C, 150 °C and 280 °C, respectively. The m/z = 149 was used to quantify both DnBP and DEHP, and the m/z = 153 was used to quantify their deuterated surrogate standards. The m/z = 233 and the m/z =267 were used for the qualitative analysis of DnBP and DEHP, respectively. The chromatograms were processed on the software of MSD ChemStation E.02.01.1177 (Agilent Technologies).

UPLC-MS/MS Instrumental analysis for MPEs

The concentrations of MPEs were analyzed on a Waters ACQUITY ultra-performance liquid chromatography (UPLC) in combination with a Waters Micromass electrospray ionization tandem mass spectrometer (ESI-MS/MS). Chromatographic separation of compounds was performed at 40 °C, using ACQUITY UPLC BEH C18 column (2.1×100 mm, 1.7 μm particle size, Waters). Mobile phase A was 0.001% formic acid in water/methanol (95/5, v/v) and mobile phase B was pure acetonitrile. The following gradient program (with respect to mobile phase A) was used: 0 0.5 min, 90 to 60% A; 0.5 4 min, 60 to 5% A; 5 6 min, 90% A; 6 7 min, re-equilibrate with 90% A. The flow rate was 0.2 ml/min, and the sample injection volume was 5 μl. Mass analysis was carried out using a Waters Micromass triple quadrupole detector equipped with an electrospray ionization (ESI) source. Data acquisition was performed in negative ESI modes and the optimized mass spectrometry (MS) parameters were as follows: source temperature, 120°C; desolvation temperature, 350 °C; capillary voltage, 3.2 kV; cone voltage, 30 V; desolvation gas flow, 600 L h^{-1} and cone gas flow, 50 L h^{-1}. The collision gas (Argon, 99.999%) flow in the collision cell was kept at 0.2 ml min^{-1}. Quantitative analysis was performed in the multiple reaction monitoring (MRM) mode and the optimized parameters are listed in Table S2. A dwell time of 0.02 s per ion pair was used. All data were acquired and processed using the MassLynx 4.1 software.

Table S1. Validation of extraction methods

Compound	LOD [a]	LOQ [b]	Concentration Range (μg L^{-1})	Linearity	Recovery in plant/cell (%, Level 1000 μg kg^{-1})	Recovery in sand (%, Level 500 μg kg^{-1})
DnBP	Plant:1.0μg kg^{-1} Sand:0.1μg kg^{-1} Cell:4.1μg kg^{-1} Medium:2.2μg L^{-1}	Plant:3.3μg kg^{-1} Sand:0.3μg kg^{-1} Cell:14μg kg^{-1} Medium:7.9μg L^{-1}	5.0 - 750	r^2=0.9987	75.0 – 86.5	75.9 – 82.3
DEHP	Plant:2.2μg kg^{-1} Sand:0.3μg kg^{-1} Cell:11μg kg^{-1} Medium:5.0μg L^{-1}	Plant:8.5μg kg^{-1} Sand:1.1μg kg^{-1} Cell:36μg kg^{-1} Medium:16μg L^{-1}	5.0 - 750	r^2=0.9990	81.3 – 101.8	81.1 – 86.7
MnBP	Plant:7.3μg kg^{-1} Sand:0.9μg kg^{-1} Cell:26μg kg^{-1} Medium:14μg L^{-1}	Plant:23μg kg^{-1} Sand:3.0μg kg^{-1} Cell:72μg kg^{-1} Medium:42μg L^{-1}	5.0 - 1000	r^2=0.9998	80.2 – 91.3	89.7 – 97.2
MEHP	Plant:3.6μg kg^{-1} Sand:0.5μg kg^{-1} Cell:15μg kg^{-1} Medium:8μg L^{-1}	Plant:11μg kg^{-1} Sand:2.0μg kg^{-1} Cell:46μg kg^{-1} Medium:27μg L^{-1}	5.0 - 1000	r^2=0.9989	78.1 – 85.8	81.9 – 92.5

a Limits of Detection (LOD) for individual PAEs/MPEs were calculated on the basis of 3 times the signal-to-noise in low-level spiked samples

b Limits of quantification (LOQ) for individual PAEs/MPEs were calculated on the basis of 10 times the signal-to-noise in low-level spiked samples

72 **Table S2.** Parameters for the analysis of MPEs and their deuterated compounds by UPLC-MS/MS.

Compound	RT (min)		Molecular Ion	Product Ion	Dwell Time (ms)	Cone voltage (V)	Collision energy (eV)
mono-*n*-Butyl Phthalate	3.31	A	221	77	80	-18	-26
		B	221	149	80	-18	-16
mono-*n*-Butyl Phthalate-*d*4	3.29	A	225	81	80	-18	-26
		B	225	153	80	-18	-16
mono-2-Ethylhexyl Phthalate	5.15	A	277	77	100	-20	-15
		B	277	134	100	-20	-23
mono-2-Ethylhexyl Phthalate-*d*4	5.12	A	281	81	100	-20	-15
		B	281	138	100	-20	-23

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75 **Table S3.** Plant biomasses per pot (gram dry weight)

Plant species	PAEs spiked group	MPEs spiked group	Control	Analysis of variance
Lettuce	3.73 ± 0.22	3.76 ± 0.17	3.76 ± 0.17	Not significant (P>0.05)
Strawberry	1.90 ± 0.15	1.76 ± 0.10	1.69 ± 0.14	Not significant (P>0.05)
Carrot	2.67 ± 0.11	2.56 ± 0.13	2.54 ± 0.06	Not significant (P>0.05)

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78 **Table S4.** Concentrations (μg kg^{-1} dry weight) of Target PAEs and MEPs in Plant Tissues at the end of treatment. Values represents means and

79 standard error of three replicates.

Compound	Lettuce		Strawberry		Carrot	
	Leaf	Root	Leaf	Root	Leaf/Stem	Root
DnBP uptake	127.5 ± 6.0	382.3 ± 42.7	171.2 ± 39.2	1306.3 ± 210.7	539.1 ± 104.3	2391 ± 293.3
DEHP uptake	653.8 ± 205.8	872.5 ± 224.9	689.1 ± 97.0	976.3 ± 205.8	1209.1 ± 230.4	1371.4 ± 92.9
MnBP uptake	1183.1 ± 50.8	1309.9 ± 271	846 ± 44.0	1329.2 ± 111.4	1236.7 ± 119.3	1606.5 ± 88.7
MEHP uptake	173 ± 49.0	329.7 ± 78.7	79.1 ± 17.1	220.4 ± 13.9	217.5 ± 23.6	236.3 ± 14.3
MnBP produced	2748.1 ± 136.5	2908.3 ± 433.2	2786.4 ± 56.2	2432.1 ± 474.2	4265.5 ± 492.4	4016.3 ± 221.9
MEHP produced	370.3 ± 146.1	422.4 ± 116.7	479.3 ± 57.0	487 ± 16.8	701.3 ± 54.0	502.2 ± 81.6

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82 **Table S5.** Physicochemical properties of PAEs and MPEs.

Phthalate Ester	Abbreviation	CAS No.	Water Solubilities mg/L	Log K_{ow}	Molecular Weight	Log *K*oa	Log D (pH 6)	pKa	References
Di-*n*-butyl Phthalate	DnBP	84-74-2	11.2	4.45	278.4	8.63			1
Di(2-ethylhexyl) Phthalate	DEHP	117-81-7	0.003	7.50	390.6	10.5			1
mono-*n*-Butyl Phthalate	MnBP	131-70-4	125.7	2.84	222.2		0.07	4.2	2
mono-2-Ethylhexyl Phthalate	MEHP	4376-20-9	1.492	4.73	278.3		1.66	4.2	2

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84 **Table S6.** PAE and MPE concentrations ($\mu g\ kg^{-1}$) in the sand at the end of treatment.

Compound	PAE spiked treatment				MPE spiked treatment			
	Lettuce group	Strawberry group	Carrot group	Spiked unplanted control	Lettuce group	Strawberry group	Carrot group	Spiked unplanted control
DnBP	173.2 ± 14	143.4 ± 8.6	133.6 ± 5.2	197 ± 12				
DEHP	216.2 ± 17	249.1 ± 14	289.3 ± 24	295 ± 11				
MnBP	82.7 ± 7.9	116.7 ± 29	77.8 ± 6.5	57.2 ± 4.5	38.9 ± 5.6	39.3 ± 6.2	42.3 ± 2.7	44.8 ± 4.1
MEHP	34.7 ± 4.3	40.0 ± 3.0	30.6 ± 2.7	27.1 ± 2.0	63.7 ± 4.2	72.1 ± 6.6	82.9 ± 6.1	90.2 ± 7.8

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88 **Table S7.** Mass balance of PAEs and MPEs (μg) spiked into sand medium growing plants for 28 d. The initial spiked amounts were 500 μg. The
89 percentage to the total spike was in the parentheses.

Compound	Lettuce group		Strawberry group		Carrot group	
	Sand medium	Plant tissue	Sand medium	Plant tissue	Sand medium	Plant tissue
DnBP	173.2 ± 14 (34.7 %)	0.88 ± 0.01 (0.2 %)	143.4 ± 8.6 (28.7 %)	1.54 ± 0.14 (0.3 %)	133.6 ± 5.2 (26.8 %)	4.17 ± 0.26 (0.1 %)
DEHP	216.2 ± 17 (43.2 %)	2.81 ± 0.68 (0.6 %)	249.1 ± 14 (49.8 %)	1.61 ± 0.21 (0.3 %)	289.3 ± 24 (57.9 %)	3.47 ± 0.37 (0.7 %)
MnBP	38.9 ± 5.6 (7.8 %)	4.62 ± 0.52 (0.9 %)	39.3 ± 6.2 (7.8 %)	2.00 ± 0.16 (0.4 %)	42.3 ± 2.7 (8.5 %)	3.64 ± 0.21 (0.7 %)
MEHP	63.7 ± 4.2 (12.8 %)	0.91 ± 0.11 (0.2 %)	72.1 ± 6.6 (14.4 %)	0.29 ± 0.03 (0.1 %)	82.9 ± 6.1 (16.6 %)	0.58 ± 0.06 (0.1 %)

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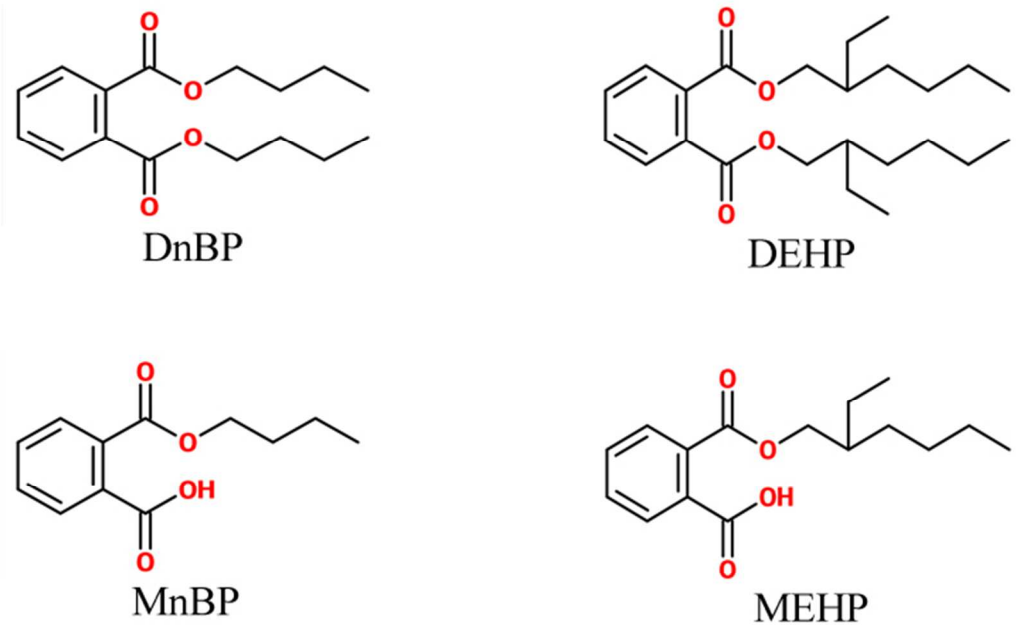

Figure S1. Chemical structures of PAEs and MPEs

Supplemental References

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