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**Supporting Information**

**Uptake, Translocation, and Biotransformation of Organophosphorus Esters in  
Wheat (*Triticum aestivum* L.)**

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**Root Exudate Control Experiments.** Root exudate controls were carried out mainly to explore the role of root exudates and microbes and were performed as follows: 15 wheat seedlings were planted in containers filled with 120 mL of sterile half-strength Hoagland nutrient solution without exposure compounds. Then solutions containing roots exudates and microbes were collected after 10 days of cultivation, replenished to 120 mL with sterile nutrient solution and spiked with OPEs with their initial concentrations at 75 µg/L and exposed for another 10 days. The treatment was sampled at 240 h.

**Extraction and Cleanup of OPE Congeners.** Before extraction, 0.3-0.8 g (dry weight) amount of plant samples or 50 mL of exposure solutions were spiked with 10 ng of surrogates d27-TnBP and d15-TPhP, then mixed and equilibrated for 24 h under a fume hood at room temperature. The plant samples were extracted with 100 mL of the mixture of dichloromethane and n-hexane (1:1, v/v) in a Soxhlet extractor for 12 h. The extracts were concentrated and then cleaned and fractionated using a 10 mm i.d. silica/alumina column. Anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) (60 mesh), silica gel and alumina (100–200 mesh) were washed with n-hexane and activated at 200 °C overnight. Florisil (100–200 mesh) was activated at 400 °C for 8 h and deactivated by adding 3% (w/w) water. The column was packed with anhydrous sodium sulfate (2 cm), neutral alumina (6 cm, 3% deactivated), neutral silica gel (8 cm, 3% deactivated), florisil (6 cm, 3% deactivated), and anhydrous sodium sulfate (2 cm) from the bottom to the top. The column was pre-rinsed with 100 mL of 1:1 (v/v) mixture of n-hexane and ethyl acetate, and then eluted with 50 mL of n-hexane:dichloromethane (1:1, v/v).

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The eluates were evaporated to approximately 5 mL, and then concentrated down to dryness under a gentle stream of nitrogen. The residue was redissolved in 200  $\mu$ L toluene and filtered using 0.22  $\mu$ m PTFE syringe filters to obtain the sample ready for GC-MS analysis. The spiked solution samples were filtered using a 0.45  $\mu$ m nylon filter and then passed through the Oasis HLB SPE cartridges (3 cm<sup>3</sup>, 60 mg, 30  $\mu$ m, Waters, Milford, MA), pre-conditioned sequentially with 3 mL methanol and 3 mL ultrapure water. The cartridges were then washed with 6 mL of ultrapure water and dried completely under vacuum. The target compounds were eluted sequentially by 3 mL of methanol and 3 mL of acetonitrile. The eluates were concentrated to 0.5 mL and centrifuged (12000 rpm, 4 °C, 30 min) before GC-MS analysis.

**Extraction and Cleanup of OPE Metabolites.** Before extraction, plant samples or solutions were spiked with 10 ng of surrogates d10-BDCPP and d10-DPhP. The extraction and cleanup procedures were the same as the parent compounds. To increase the retention and sensitivity of the metabolites on the GC-MS system, derivatization was performed before analysis. The procedure for derivatization was based on the method of Schindler et al.<sup>1</sup> with some modifications. Five gram of pentafluorobenzyl bromide (PFBBr) was diluted in 6 mL of acetonitrile as reagent for derivatization. The eluates contained the target compounds were evaporated to dryness at 50 °C under a gentle stream of nitrogen. The residue was redissolved in 1 mL acetonitrile, then 10 mg potassium carbonate and 100  $\mu$ L pentafluorobenzyl bromide derivatization solution were added and vortex mixed. The derivatization took place at 60 °C within 16 h. The samples were cooled down to room temperature and

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vortex mixed. After evaporation to dryness, the residue was reconstituted in 5 mL hexane and transferred to a second SPE step. Two SPE cartridges were connected by an adapter, Bond Elut PSA (500 mg, 3 mL, anion exchange material, Varian Inc., Middelburg, Netherlands) at the top and Bond Elut FL (500 mg, 3 mL, florisil, Varian Inc., Middelburg, Netherlands) on the bottom. The cartridges were conditioned with 3 mL hexane and loaded with the hexane extracts. Then the cartridges were washed with 3 mL hexane and the analytes were eluted with 6 mL acetone and hexane mixture (1:1, v/v). The eluates were then concentrated down to dryness. The residue was re-dissolved in 200  $\mu$ L of toluene and filtered using 0.22  $\mu$ m PTFE syringe filters to obtain the sample ready for GC-MS analysis. To prevent possible photolysis, all the glasses used for sample extraction and cleanup were wrapped with aluminum-foil paper. To minimize the potential contamination and possible degradation of OPEs, proper handling was employed from sample collection to chemical analysis. All glass containers were burned at high temperature (500  $^{\circ}$ C) for 6 to 8 h and rinsed with n-hexane and acetone to avoid contamination.

**Analysis of OPE Congeners and Metabolites.** OPEs were separated with a HP-5MS column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m) (Agilent J&W Scientific) and analyzed by an Agilent 7890A chromatography-mass spectrometry system (5975C Inert) (Agilent, Palo Alto). The MS were operated in selected ion monitoring (SIM) mode under EI ionization for quantitation. Helium was used as the carrier gas at a flow rate of 1.5 ml/min. The oven temperature program was as follows: 1 min at 50  $^{\circ}$ C, first ramp at 10  $^{\circ}$ C/min to 200  $^{\circ}$ C (1 min hold), second ramp at 3  $^{\circ}$ C/min to 260  $^{\circ}$ C (5 min hold).

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The injected volume was 1  $\mu\text{L}$ , and the injection-port temperature was 280  $^{\circ}\text{C}$  in the splitless mode. The electron energy was set at 70 eV, and the ion source temperature was 230  $^{\circ}\text{C}$ .

Quantification of the metabolites including BCEP, BCPP, BDCPP, BBEP, DiBP, DnBP, DPhP, MnBP and MPhP was performed on GC-MS (Agilent J&W Scientific) under the SIM mode with a DB-35MS column (60 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). The oven temperature program was as follows: 1 min at 70  $^{\circ}\text{C}$ , first ramp at 5  $^{\circ}\text{C}/\text{min}$  to 110  $^{\circ}\text{C}$  (3 min hold), second ramp at 10  $^{\circ}\text{C}/\text{min}$  to 290  $^{\circ}\text{C}$  (3 min hold). The injected volume, injection-port temperature, electron energy, and the ion source temperature were the same as parent compounds. Possible metabolites of OPEs which have no corresponding commercial standards were identified by UHPLC coupled with electrospray ionization quadrupole time-of-flight tandem mass spectrometry (ESI-Q-TOF-MS) (Agilent Technologies, Santa Clara, CA). Chromatographic separation of the metabolites was achieved using a BEH C18 column (50 mm  $\times$  2.1 mm  $\times$  1.7  $\mu\text{m}$ , Waters) and following mobile phase composition: 5 mM ammonium acetate in water (A) and methanol (B). Gradient elution was as follows: 10% B from 0 to 0.5 min, linear increase of B to 95% from 0.5 to 10 min, followed by isocratic elution at 95% B from 10 to 12 min, linear decreased to 10% of B from 12 to 13 min and maintained at 10% from 13 to 15 min to re-equilibrate the column. The flow rate was 0.15 mL/min and the injection volume was 20  $\mu\text{L}$ . Total run time was 15 min. The Q-TOF-MS was performed in ESI negative mode scanning  $m/z$  from 50 to 1000 amu at a scan rate of 1.25 spectra/s for both MS and MS/MS acquisition. The main

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instrument setting for the Q-TOF was as follows: drying gas temperature 300 °C, drying gas flow 10 L/min, nebulizer pressure 35 psi, collision flow 22 psi, sheath gas temperature 325 °C, sheath gas flow 15 L/min. Nozzle, capillary, fragmentor, skimmer voltages, OCT 1 RF Vpp, and collision energy were set to 500 V, 3000 V, 130 V, 65 V, 750 V, 10 V, respectively. The m/z values of potential candidates were assigned according to their retention time. The assignment of the chemical formula was accomplished according to the following criteria: the deviation for ion mass was set to < 10 ppm<sup>2</sup> and the following element limits, C (0-100), H (0-100), O (0-30), P (0-2), S (0-2), and Cl (0-6). The semi-quantitative concentrations of the metabolites were determined by using peak area.

**Quality Assurance/Quality Control (QA/QC).** Quality control was performed by regular analysis of the procedural blanks, blind duplicate samples, and random injection of solvent blanks and standards. Recoveries were obtained by the addition of OPE standards, surrogate standards and metabolites individually to the untreated plant controls and nutrient solutions before extraction and analysis. In detail, 20.0, 100.0 and 500.0 ng of standards of 20.0, 100.0 and 500.0 ng in methanol at concentration of 1 mg/mL (volumes of 20, 100 and 500 µL, respectively) were spiked into the dried plant materials or solution separately and then equilibrated for 24 h for solvent volatilization. Preliminary experiment has shown that methanol added at these concentrations as solvent does not influence the sorption of the standards on plant materials. The spiked samples were then analyzed in triplicate using the method performed in this study. Recoveries of OPEs were 75.6-90.0% for plant samples, and

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80.2%-104.5% for solution samples. Recoveries of the metabolites in plant tissues and solutions were 71.3%-82.4% and 77.9%-92.1%, respectively. Recoveries of surrogate standard were as follows: 77.4-86.5% for d27-TnBP, 79.7-89.6% for d15-TPhP, 76.2-85.7% for d10-BDCPP and 73.5-82.8% for d10-DPhP. The limits of detection (LODs), defined as the lowest concentration level corresponding to a signal-to-noise (S/N) ratio of 3, were determined as 0.06-0.35 ng/g in plants and 1.2-75 ng/L in solutions. The intra-day and inter-day relative standard deviations (RSD) were both below 10%.

**Enzyme Assays.** Wheat roots were carefully rinsed with sterile water and finely chopped. Approximately 1 g of fresh root samples were homogenized on ice with 4 mL of extraction buffer (pH 7.8) containing 0.05 M  $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ , 2 mM EDTA, 1% (w/v) polyvinylpyrrolidone and 2 mM dithiothreitol. After centrifugation at 12000 rpm at 4 °C for 15 min, the supernatant was collected for further analysis. The protein level was measured by the Bradford method<sup>3</sup> using bovine serum albumin as the standard. GST activity was determined based on the method described by Habig et al.<sup>4</sup> The reaction mixture contained 1.0 mM 1-chloro-2,4-dinitrobenzene (CDNB), 5.0 mM glutathione (GSH), and 100  $\mu\text{L}$  of protein extract in phosphate buffered saline (PBS, pH 6.5) in a final volume of 3.0 mL. The change in absorbance of CDNB-GSH conjugate was measured at 25 °C for 5 min at 340 nm. The enzyme activity was calculated using an extinction coefficient of  $9.6 \text{ mM}^{-1} \cdot \text{cm}^{-1}$ . CYP450 activity was assayed with the Plant CYP450 ELISA Kit (Dongge Biotechnology Co. Ltd, Beijing, China). The color change was measured spectrophotometrically at a

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wavelength of 450 nm. All the enzyme activities are expressed as U·mg<sup>-1</sup> protein.

**Gene Expression Assays.** Total RNA was isolated from liquid nitrogen frozen wheat roots (100 mg), followed by precipitation with lithium chloride and then isopropanol, and then the sample was resuspended in 300 µL sterile water. Poly(A)<sup>+</sup> mRNA was isolated from the total RNA using a QuickPrep Micro mRNA Purification Kit (Amersham Pharmacia Biotech) as outlined in the manufacturer's directions. The mRNA was resuspended in sterile water and stored at -80 °C. Typically, 1 µg of mRNA was recovered from 100 mg of wheat roots. Single-stranded cDNAs were synthesized from 1 µg of Poly(A)<sup>+</sup> mRNA with a Bio-Rad iQ5 System (Bio-Rad Company, CA) and used as templates for quantitative real-time PCR (qRT-PCR). The primer sequences for the PCRs of CYP450 were based on the published sequence data for the wheat proteins CYP71C6V1,<sup>5,6</sup> and primer sequences for GST were designed by Primer Premier 5.0 according to the wheat GSTA1 gene for glutathione-S-transferase (Genbank Accession No.: X56012). Wheat mitochondrion 26s rRNA (Genbank Accession No.: Z11889.1) was used as internal standard. The qRT-PCRs were carried out in a 50 µL mixture containing 50 ng of template, 100 pmol of primers (Table S4), 0.2 mM dNTPs, 3.5 mM MgCl<sub>2</sub>, and 10% DMSO. After an initial incubation for 5 min at 94 °C, 30 cycles of amplification were carried as follows: 1 min denaturation at 94 °C, 2 min annealing at 55 °C, 3 min extension at 72 °C. The reaction was completed by 10 min of extension at 72 °C. The relative expression was normalized based on these two genes by  $\Delta\Delta C_t$  method using the CFX Manager software (Bio-Rad).

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**Homology Modeling and Molecular Docking.** *TaLTP1.1*, *TaGST4-4* and CYP71C6v1 in wheat were chosen to investigate the interaction between OPEs and biomacromolecules. The 3-D structures of the proteins *TaLTP1.1* and *TaGST4-4* are available in the Protein Data Bank (PDB) with entry codes 1CZ2 and 1GWC, respectively. The 3-D structure of CYP71C6v1 was constructed by homology modeling. The primary sequences of CYP71C6v1 are available at the National Center for Biotechnology Information (NCBI) Web site (<http://www.ncbi.nlm.nih.gov>). The template proteins 3PM0 (Human CYP1B1, resolution: 2.70 Å) identified by the BLAST program (<http://blast.ncbi.nlm.nih.gov/Blast.cgi>) was employed as the template for CYP71C6v1. The sequence identity was 25% for CYP71C6v1 to CYP1B1 (Figure S1A). The initial 3-D structural model was energy-minimized to release the poor atomic contacts and tune unreasonable local structural conformations. The overall geometric and stereochemical qualities of the homology models were assessed using Protein Geometry. Ramachandran plots for all of the residues in each model were checked and adjusted by energy minimization. Result showed that the percentage of the residues in the core Ramachandran region were 91.8% for CYP71C6v1 (Figure S1B). Residues located in the unfavorable regions were far from the substrate-binding domain, implying negligible influence on the ligand-protein binding simulations. This suggests that the models of the plant enzymes are of reasonable quality compared with the crystal structures of the templates. *TaLTP1.1* contained four  $\alpha$  helices and random coils. *TaGST4-4* contained nine  $\alpha$  helices, four  $\beta$  sheets and random coils (Figure S1C). CYP71C6v1 contained nine  $\alpha$  helices, nine  $\beta$

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sheets and random coils. Molecular docking was carried out to simulate the detailed binding modes of OPEs to biomacromolecules using Autodock 4.2. Prior to analysis, the structural models of OPEs were generated by ChemDraw 11.0 (Cambridge Soft, Waltham, MA) and energies minimized using the molecular mechanics method (MM2). Polar hydrogen atoms were added and Kollman charges were assigned to all atoms of the proteins. Then, Gasteiger charges were added and nonpolar hydrogen atoms were merged for the ligand. A  $40 \times 40 \times 40 \text{ \AA}$  3-D affinity grid centered around the binding active site with  $0.375 \text{ \AA}$  spacing between grid points. The Lamarckian genetic algorithm (LGA) was used for ligand conformation and all bond rotations for ligands were ignored. The maximum number of top individuals, the rate of gene mutation, and crossover were set as default values. The MOLDOCK score algorithm was employed to calculate the energetic evaluations and to select the best orientation with the highest docking score. The lowest energy docking models were selected from the fine grid docking.

**Table S1** Names, abbreviations, formulas and properties of the OPEs and metabolite standards involved in the present study

Acronym	Name	Formulae	log $K_{ow}$	Water solubility (mg/L) (25 °C)
Tri-esters				
Halogenated OPEs				
TCEP	Tri(2-chloroethyl) phosphate	C <sub>6</sub> H <sub>12</sub> Cl <sub>3</sub> O <sub>4</sub> P	1.44	7.0×10 <sup>3</sup>
TCPP	Tri(1-chloro-2-propyl) phosphate	C <sub>9</sub> H <sub>18</sub> Cl <sub>3</sub> O <sub>4</sub> P	2.59	1.6×10 <sup>3</sup>
TDCPP	Tri(1,3-dichloro-2-propyl) phosphate	C <sub>9</sub> H <sub>15</sub> Cl <sub>6</sub> O <sub>4</sub> P	3.65	1.5
Non-halogenated alkyl OPEs				
TiBP	Tri-iso-butyl phosphate	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P	3.6	3.72
TnBP	Tri-n-butyl processes phosphate	C <sub>12</sub> H <sub>27</sub> O <sub>4</sub> P	4.0	280
TBEP	Tri(2-butoxyethyl) phosphate	C <sub>18</sub> H <sub>39</sub> O <sub>7</sub> P	3.75	1.2×10 <sup>3</sup>
Non-halogenated aryl OPEs				
TPhP	Tri-phenyl phosphate	C <sub>18</sub> H <sub>15</sub> O <sub>4</sub> P	4.59	1.9
EHDPP	2-Ethylhexyl di-phenyl phosphate	C <sub>20</sub> H <sub>27</sub> O <sub>4</sub> P	5.73	1.9
Metabolites				
Di-esters				
BCEP	Bis(2-chloroethyl) phosphate	C <sub>4</sub> H <sub>9</sub> Cl <sub>2</sub> O <sub>4</sub> P	-	-

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BCPP	Bis(1-chloro-2-propyl) phosphate	$C_6H_{13}Cl_2O_4P$	-	-
BDCPP	Bis(1,3-dichloro-2-propyl) phosphate	$C_6H_{11}Cl_4O_4P$	-	-
DiBP	Di-iso-butyl phosphate	$C_8H_{19}O_4P$	-	-
DnBP	Di-n-butyl phosphate	$C_8H_{19}O_4P$	-	-
BBEP	Bis(2-butoxyethyl) phosphate	$C_{12}H_{27}O_6P$	-	-
DPhP	Di-phenyl phosphate	$C_{12}H_{11}O_4P$	-	-
Mono-esters				
MnBP	Mono-n-butyl phosphate	$C_4H_{11}O_4P$	-	-
MPhP	Mono-phenyl phosphate	$C_6H_7O_4P$	-	-
Isotope-labeled standards				
d27-TnBP	Tri-n-butyl phosphate-d27	$C_{12}D_{27}O_4P$	-	-
d15-TPhP	Tri-phenyl phosphate-d15	$C_{18}D_{15}O_4P$	-	-
d10-BDCPP	Bis(1,3-dichloro-2-propyl) phosphate-d10	$C_6HCl_4D_{10}O_4P$	-	-
d10-DPhP	Di-phenyl phosphate-d10	$C_{12}HD_{10}O_4P$	-	-

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The data are compiled from previous studies (World Health Organization, 1991, 1998; Marklund et al., 2003; Van der Veen and De Boer, 2012; Quintana et al., 2006; Dodson et al., 2014).<sup>7-12</sup>

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**Table S2** The GC-MS operational parameters of the target compounds and surrogates.

The metabolites were derivatized before analysis

Compounds	Molecular ion (m/z)	Qualitative ion (m/z)	Quantitative ion (m/z)
TCEP	285.5	249.0	204.9
T CPP	327.6	157.0	125.0
TDCPP	430.9	75.0	190.9
TBEP	398.5	199.1	227.1
TiBP	266.3	99.0	155.0
TnBP	266.3	99.0	155.0
EHDPP	362.4	94.1	251.1
TPhP	326.3	77.1	170.0
BCEP	403.0	222.0	339.0
BCPP	431.0	99.0	251.0
BDCPP	499.9	190.9	319.0
BBEP	478.3	199.1	297.1
DnBP	390.2	99.0	209.0
DiBP	390.2	99.0	209.0
DPhP	430.2	249.0	317.0
MnBP	514.1	79.1	153.1
MPhP	534.1	79.1	173.1
d15-TPhP	341.9	369.9	341.9
d27-TnBP	293.2	166.0	230.0
d10-BDCPP	510.0	329.0	327.0
d10-DPhP	440.3	259.0	178.0

**Table S3** Rescoveries and LODs of OPEs and metabolites in plant and solution samples

Compounds	Recovery (%)		LOD	
	Solutions	Wheat tissues	Solutions (ng/L)	Wheat tissues (ng/g)
TCEP	94.2 ± 2.1	84.7 ± 2.7	1.2	0.06
TCPP	96.9 ± 2.7	82.6 ± 2.2	10	0.09
TDCPP	95.7 ± 2.1	84.2 ± 3.2	6	0.08
TBEP	81.7 ± 1.6	76.4 ± 1.1	44	0.2
TiBP	90.8 ± 1.3	78.9 ± 2.1	28	0.12
TnBP	92.1 ± 4.1	81.6 ± 2.2	15	0.1
EHDPP	99.5 ± 4.4	88.2 ± 2.4	35	0.15
TPhP	92.7 ± 1.5	85.1 ± 3.4	40	0.18
BCEP	90.9 ± 1.2	75.1 ± 1.9	32	0.15
BCPP	90.1 ± 1.8	76.9 ± 1.9	42	0.22
BDCPP	87.6 ± 2.8	78.4 ± 1.5	25	0.1
BBEP	81.5 ± 3.2	74.1 ± 2.7	75	0.35
DnBP	82.8 ± 2.6	73.5 ± 1.6	56	0.25
DiBP	84.8 ± 2.6	77.4 ± 1.1	62	0.3
DPhP	89.2 ± 1.5	81.3 ± 1.0	24	0.12
MnBP	85.3 ± 1.9	75.7 ± 2.0	60	0.3
MPhP	87.2 ± 2.1	80.2 ± 1.7	36	0.18

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**Table S4** qRT-PCR primers for CYP71C6V1, *Ta*GST4-4 and internal standard

Primer	Target	Sequence (5'-3')
26s-FW	26s rRNA	GAAGAAGGTCCCAAGGGTTC
26s-RV		TCTCCCTTTAACACCAACGG
CYP-FW	CYP71C6V1	TATATAGAATTCCAGTTA
CYP-RV		ATGGCTCTTGAAGCAGCG
GST-FW	<i>Ta</i> GST4-4	ATGTCTCCGGTGAAGGTG
GST-RV		CTAGTACTGCGCACCTAG

**Table S5** Concentrations of OPEs and metabolites in blank controls

Compounds	Untreated plant control				Unplanted control		
	Solution ( $\mu\text{g/L}$ )	Root ( $\text{ng/g}$ )	Shoot ( $\text{ng/g}$ )	Metabolites ( $\text{ng/g}$ )	Initial concentration ( $\mu\text{g/L}$ )	Final concentration ( $\mu\text{g/L}$ )	Metabolites ( $\mu\text{g/L}$ )
TCEP	N.D. <sup>a</sup>	N.D.	N.D.	N.D.	75.4 $\pm$ 2.1	73.5 $\pm$ 3.4	N.D.
TCPP	N.D.	N.D.	1.89	N.D.	74.3 $\pm$ 1.6	69.7 $\pm$ 2.2	N.D.
TDCPP	N.D.	N.D.	N.D.	N.D.	76.9 $\pm$ 3.3	72.3 $\pm$ 4.5	N.D.
TBEP	N.D.	N.D.	1.02	N.D.	73.5 $\pm$ 2.5	67.6 $\pm$ 3.7	N.D.
TiBP	N.D.	N.D.	N.D.	N.D.	72.0 $\pm$ 4.2	67.8 $\pm$ 1.6	N.D.
TnBP	N.D.	N.D.	N.D.	N.D.	71.6 $\pm$ 1.9	67.1 $\pm$ 2.4	N.D.
TPhP	N.D.	N.D.	N.D.	N.D.	75.6 $\pm$ 3.8	71.8 $\pm$ 3.1	N.D.
EHDPP	N.D.	N.D.	N.D.	N.D.	74.0 $\pm$ 1.7	69.4 $\pm$ 1.2	N.D.

<sup>a</sup> Not detected.

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**Table S6** The average and maximum measured TSCFs and the predicted data of OPEs

Compounds	Log $K_{ow}$	Maximun TSCF value	Average TSCF value	Predicted data from the model <sup>a</sup>
TCEP	1.44	0.70	0.46	0.73
TCPP	2.59	0.42	0.26	0.47
TDCPP	3.65	0.22	0.15	0.24
TBEP	3.75	0.28	0.20	0.23
TiBP	3.6	0.19	0.13	0.25
TnBP	4.0	0.23	0.15	0.20
TPhP	4.59	0.12	0.075	0.12
EHDPP	5.73	0.05	0.03	0.05

<sup>a</sup> Calculated using the relationships developed by Dettenmaier et al.<sup>13</sup>

**Table S7** Mass composition of OPEs and quantified metabolites in root exudate controls<sup>a</sup>

Compounds	Root exudate group			Recovery (%)
	Parents (%)	Di-esters (%)	Mono-esters (%)	
TCEP	87.5±6.8 <sup>b</sup>	5.97±0.5	N.A. <sup>c</sup>	93.5±8.3
TCPP	82.2±6.2	5.26±0.5	N.A.	87.5±6.5
TDCPP	81.4±4.4	8.98±0.5	N.A.	90.4±4.6
TBEP	62.1±5.2	12.4±0.9	N.A.	74.3±7.6
TiBP	68.9±5.5	10.6±1.8	N.A.	79.1±8.1
TnBP	70.9±4.5	13.5±1.4	2.61±0.2	86.5±5.9
TPhP	74.3±6.4	6.83±0.3	1.31±0.2	82.5±6.7
EHDPP	70.8±6.1	11.3±1.4	2.48±0.2	84.8±7.8

<sup>a</sup> The percentage of OPEs and metabolites in solution and wheat plant to the initial amount of OPEs applied.

<sup>b</sup> Standard deviation for triplicate measurements.

<sup>c</sup> Not available for lack of the commercial standards.

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**Table S8** The logRCF values of the metabolites and their corresponding parent compounds

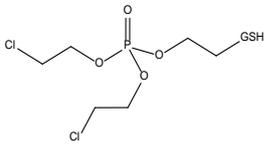
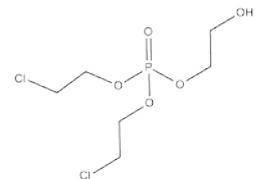
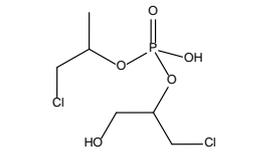
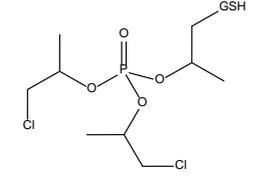
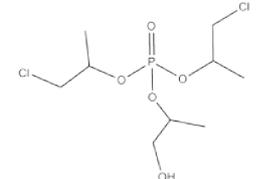
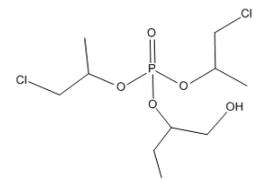
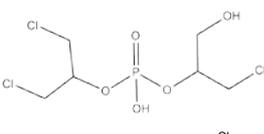
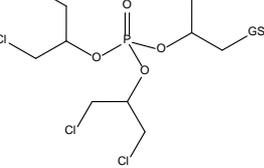
Metabolites	Average logRCF	Parent Compounds	Average logRCF
BCEP	3.16	TCEP	1.67
BCPP	3.18	TCPP	1.97
BDCPP	3.22	TDCPP	2.31
BBEP	2.89	TBEP	2.77
DiBP	3.16	TiBP	2.43
DnBP	3.03	TnBP	2.53
DPhP(TPhP)	3.59	TPhP	3.03
DPhP(EHDPP)	3.70	EHDPP	3.50
MnBP	2.90	TnBP	2.53
MPhP(TPhP)	3.57	TPhP	3.03
MPhP(EHDPP)	3.82	EHDPP	3.50

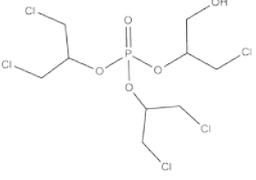
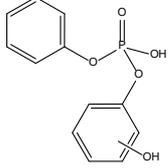
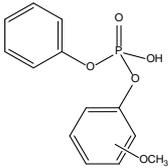
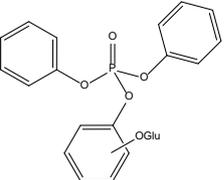
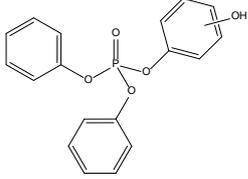
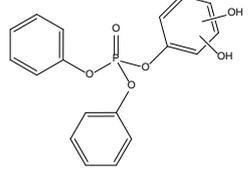
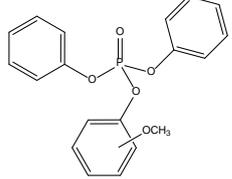
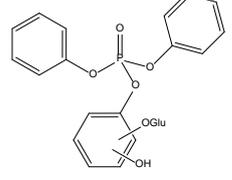
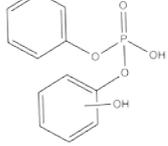
**Table S9** Mass composition of OPEs and quantified metabolites in plant exposure groups during exposure time

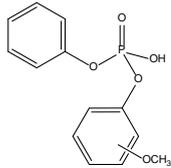
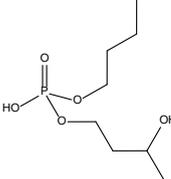
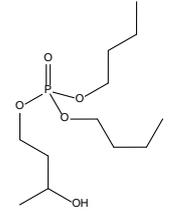
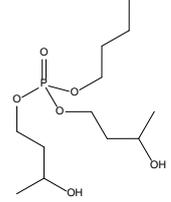
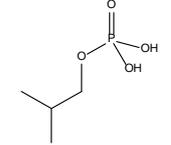
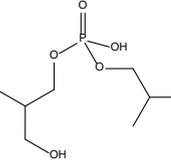
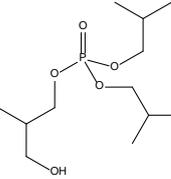
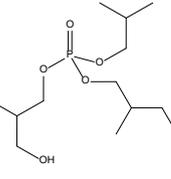
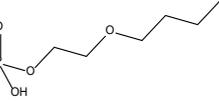
Compounds	Time(h)	Accumulation			Metabolism						Recovery(%)
		Solution(%)	Root(%)	Shoot(%)	Di-esters			Mono-esters			
					Solution(%)	Root(%)	Shoot(%)	Solution(%)	Root(%)	Shoot(%)	
TCEP	12	88.3±7.2 <sup>b</sup>	3.82±0.2	2.40±0.1	0.21±0.02	0.62±0.06	0.25±0.05	N.A.	N.A.	N.A.	95.8±8.9
	24	83.9±6.7	4.77±0.2	3.95±0.3	0.37±0.1	0.96±0.07	0.76±0.1	N.A.	N.A.	N.A.	94.7±8.9
	36	78.4±6.5	6.70±0.3	5.60±0.3	0.49±0.1	1.71±0.2	1.45±0.1	N.A.	N.A.	N.A.	94.3±9.1
	48	71.2±5.2	8.91±0.6	8.08±0.5	0.78±0.2	2.85±0.3	2.79±0.2	N.A.	N.A.	N.A.	94.6±8.6
	72	64.1±4.4	10.4±0.4	10.9±0.6	1.51±0.3	3.63±0.4	4.05±0.4	N.A.	N.A.	N.A.	94.6±6.1
	96	60.5±4.1	9.73±0.6	9.73±0.9	1.82±0.4	5.28±0.3	5.21±0.6	N.A.	N.A.	N.A.	92.2±5.3
	144	58.5±2.4	8.54±0.8	8.27±0.4	2.35±0.4	5.86±0.2	6.16±0.5	N.A.	N.A.	N.A.	89.5±4.8
	192	56.4±3.7	6.79±0.4	7.06±0.4	2.74±0.8	6.39±0.3	7.15±0.6	N.A.	N.A.	N.A.	86.4±5.2
	240	54.8±3.2	5.11±0.4	6.02±0.3	2.87±0.7	6.91±0.4	7.69±0.3	N.A.	N.A.	N.A.	83.5±3.7
TCPP	12	80.7±5.2	7.66±0.3	3.06±0.2	0.21±0.02	0.86±0.04	0.36±0.02	N.A.	N.A.	N.A.	93.0±7.7
	24	73.9±6.0	13.9±0.9	5.80±0.5	0.32±0.03	1.08±0.07	0.79±0.05	N.A.	N.A.	N.A.	95.8±8.2
	36	69.5±5.7	15.9±1.2	7.89±0.6	0.57±0.1	1.97±0.1	1.41±0.09	N.A.	N.A.	N.A.	97.9±7.3
	48	61.9±5.8	17.8±1.3	8.55±0.8	0.81±0.2	2.61±0.3	1.86±0.1	N.A.	N.A.	N.A.	93.4±8.1
	72	59.5±4.4	15.1±1.8	8.16±0.7	1.18±0.2	3.41±0.4	2.96±0.3	N.A.	N.A.	N.A.	90.5±6.0
	96	54.2±3.3	13.5±0.8	7.61±0.6	1.57±0.2	4.48±0.2	3.75±0.2	N.A.	N.A.	N.A.	85.7±6.8
	144	51.2±3.2	11.7±0.7	6.93±0.4	1.83±0.1	5.17±0.4	4.53±0.3	N.A.	N.A.	N.A.	81.2±4.2
	192	48.3±4.1	8.07±0.7	5.70±0.5	2.19±0.2	5.65±0.5	4.90±0.5	N.A.	N.A.	N.A.	75.4±5.3
	240	45.7±3.5	6.51±0.4	4.18±0.3	2.37±0.5	6.15±0.3	5.45±0.3	N.A.	N.A.	N.A.	70.5±4.1
TDCPP	12	75.7±6.8	13.8±1.2	1.60±0.1	0.10±0.01	0.52±0.03	0.27±0.02	N.A.	N.A.	N.A.	91.9±8.9
	24	67.1±5.5	21.8±1.9	2.59±0.1	0.22±0.02	0.86±0.07	0.44±0.07	N.A.	N.A.	N.A.	92.9±7.6
	36	55.5±3.2	33.7±2.4	4.37±0.2	0.46±0.06	1.47±0.1	0.94±0.07	N.A.	N.A.	N.A.	96.6±6.5
	48	48.5±4.3	32.1±2.1	6.56±0.3	1.35±0.1	3.75±0.2	1.71±0.1	N.A.	N.A.	N.A.	94.3±5.4
	72	45.3±3.6	29.2±2.0	6.08±0.5	2.34±0.3	5.38±0.2	1.84±0.1	N.A.	N.A.	N.A.	90.2±6.3
	96	44.1±2.7	24.5±1.6	5.51±0.4	3.41±0.5	7.37±0.3	3.36±0.2	N.A.	N.A.	N.A.	88.6±4.2
	144	39.7±2.8	20.6±1.2	5.04±0.3	3.51±0.5	10.9±0.8	5.05±0.3	N.A.	N.A.	N.A.	84.4±5.3
	192	37.1±3.2	13.5±1.3	3.81±0.1	3.97±0.6	14.2±1.2	7.42±0.4	N.A.	N.A.	N.A.	79.8±6.6
	240	34.3±3.3	10.8±0.8	2.19±0.2	4.11±0.5	13.2±0.9	6.26±0.6	N.A.	N.A.	N.A.	70.9±5.8
TBEP	12	48.5±3.5	37.8±3.2	6.28±0.6	2.44±0.1	3.38±0.3	0.67±0.02	N.A.	N.A.	N.A.	99.1±5.6
	24	40.5±3.4	42.0±3.6	7.42±0.3	2.77±0.2	4.62±0.2	0.93±0.06	N.A.	N.A.	N.A.	98.2±6.2
	36	34.1±2.8	45.2±2.7	7.63±0.5	4.94±0.3	7.05±0.5	2.68±0.1	N.A.	N.A.	N.A.	101.6±8.3
	48	25.4±1.6	35.6±2.8	6.84±0.2	6.79±0.5	9.22±0.6	3.39±0.2	N.A.	N.A.	N.A.	87.3±5.4
	72	20.8±1.5	39.0±3.5	6.37±0.5	8.01±0.5	10.9±0.8	3.96±0.3	N.A.	N.A.	N.A.	90.9±6.5
	96	17.1±1.2	31.7±2.1	6.65±0.4	8.30±0.7	13.4±0.8	4.43±0.3	N.A.	N.A.	N.A.	81.4±5.1
	144	13.9±1.0	22.4±2.0	5.61±0.3	8.67±0.6	16.9±1.3	5.41±0.1	N.A.	N.A.	N.A.	72.3±4.7
	192	10.7±1.0	17.2±1.4	3.56±0.1	8.03±0.4	14.2±1.2	4.09±0.2	N.A.	N.A.	N.A.	57.5±4.3
	240	8.14±0.6	10.9±1.1	1.95±0.2	7.61±0.5	12.5±1.2	3.13±0.2	N.A.	N.A.	N.A.	44.4±3.5
TiBP	12	64.6±6.1	23.7±2.3	3.25±0.3	0.67±0.1	3.20±0.2	0.41±0.02	N.A.	N.A.	N.A.	95.7±8.9
	24	57.9±2.3	27.8±1.6	4.42±0.3	1.34±0.1	6.00±0.3	0.80±0.05	N.A.	N.A.	N.A.	98.1±6.7

	36	48.5±4.5	31.9±2.7	5.05±0.4	2.02±0.1	6.89±0.5	0.91±0.06	N.A.	N.A.	N.A.	95.2±8.3
	48	41.2±3.8	27.4±1.8	5.60±0.5	1.78±0.2	8.09±0.4	2.42±0.1	N.A.	N.A.	N.A.	86.4±7.2
	72	34.9±2.6	24.7±2.2	4.15±0.1	3.08±0.3	9.41±0.6	3.65±0.2	N.A.	N.A.	N.A.	79.9±6.9
	96	31.4±2.3	20.6±1.5	3.52±0.2	6.41±0.6	12.9±1.3	3.98±0.1	N.A.	N.A.	N.A.	78.8±6.1
	144	25.9±1.8	15.8±1.4	2.80±0.1	7.11±0.9	15.3±1.1	5.63±0.3	N.A.	N.A.	N.A.	72.9±5.4
	192	20.4±1.9	12.4±1.2	2.17±0.2	7.44±1.2	14.3±0.9	4.75±0.4	N.A.	N.A.	N.A.	61.3±4.8
	240	15.1±2.0	6.5±0.5	1.42±0.1	6.73±1.1	13.1±1.2	3.18±0.3	N.A.	N.A.	N.A.	46.2±4.1
TnBP	12	58.7±5.2	30.1±2.5	4.53±0.2	0.82±0.1	2.56±0.1	0.50±0.02	0.28±0.03	0.32±0.01	0.06±0.002	98.2±8.7
	24	45.3±4.3	39.5±3.6	7.07±0.5	0.97±0.1	3.47±0.2	0.83±0.03	0.50±0.02	0.72±0.03	0.12±0.02	98.9±9.6
	36	41.4±3.2	37.5±1.7	5.89±0.1	2.26±0.4	5.30±0.2	2.13±0.1	0.70±0.04	1.16±0.06	0.44±0.03	96.7±7.9
	48	37.6±3.7	31.9±2.3	5.30±0.2	4.40±0.3	8.29±0.6	2.57±0.2	1.16±0.1	1.82±0.1	0.80±0.05	93.8±6.8
	72	32.3±2.7	26.6±1.5	3.75±0.3	5.21±0.4	12.4±1.3	4.47±0.1	1.58±0.2	2.87±0.2	1.10±0.1	90.5±5.2
	96	27.5±2.1	21.1±1.2	3.91±0.4	6.37±0.5	14.7±1.2	5.75±0.3	2.19±0.1	3.69±0.3	1.66±0.2	86.5±7.4
	144	22.2±1.9	16.8±1.3	2.93±0.3	7.68±0.5	17.2±1.1	6.69±0.6	3.10±0.1	5.29±0.3	2.90±0.2	83.8±4.1
	192	20.7±1.8	12.6±0.9	1.96±0.2	6.92±0.8	14.9±1.0	5.59±0.4	3.37±0.2	6.28±0.5	4.01±0.5	77.6±3.8
	240	18.7±1.3	7.93±0.3	1.29±0.1	11.1±0.9	12.0±0.9	4.38±0.2	3.46±0.4	7.40±0.4	5.43±0.3	68.6±2.9
TPhP	12	35.3±3.2	57.7±4.8	2.01±0.1	0.13±0.02	2.57±0.2	0.43±0.02	N.D.	0.35±0.01	0.17±0.02	98.6±9.1
	24	30.3±2.7	54.4±3.9	2.83±0.2	0.24±0.01	5.05±0.1	0.59±0.03	0.02±0.002	0.50±0.02	0.28±0.03	94.2±8.3
	36	27.3±2.6	49.7±4.2	4.11±0.2	0.34±0.01	7.11±0.3	1.29±0.09	0.06±0.005	0.77±0.02	0.45±0.03	91.2±7.7
	48	22.8±1.5	51.5±3.7	3.89±0.1	0.72±0.04	8.25±0.4	1.68±0.1	0.11±0.01	0.98±0.09	0.58±0.02	89.5±7.0
	72	20.3±1.8	49.5±3.5	3.38±0.3	1.14±0.1	9.36±0.3	1.85±0.2	0.24±0.01	1.22±0.1	0.88±0.06	86.9±5.6
	96	17.5±1.2	44.3±4.1	2.70±0.2	1.85±0.2	10.5±1.1	2.44±0.1	0.32±0.02	1.81±0.1	0.92±0.05	80.4±6.3
	144	15.7±1.3	40.0±2.6	2.20±0.2	2.08±0.2	13.1±1.0	3.12±0.2	0.56±0.05	2.98±0.2	1.04±0.06	78.8±4.0
	192	13.0±1.0	35.9±2.1	1.96±0.2	1.84±0.1	11.7±0.9	2.61±0.1	0.73±0.06	3.67±0.4	1.18±0.04	70.6±5.1
	240	11.6±0.9	29.6±2.4	1.07±0.1	1.63±0.1	9.62±1.1	2.11±0.3	0.81±0.1	4.70±0.4	1.27±0.1	60.5±3.9
EHDPP	12	23.1±2.3	70.5±5.6	1.20±0.1	0.27±0.01	4.01±0.2	0.33±0.01	N.D.	0.36±0.05	0.10±0.01	99.5±8.5
	24	18.6±1.5	66.8±4.1	1.81±0.2	0.65±0.03	7.55±0.5	0.81±0.06	N.D.	0.44±0.1	0.20±0.02	97.7±5.6
	36	14.9±1.0	64.4±6.2	2.41±0.2	0.87±0.02	11.7±0.4	1.12±0.1	0.04±0.002	0.66±0.1	0.25±0.01	96.6±7.8
	48	11.1±0.6	59.9±5.3	3.03±0.2	1.53±0.1	14.2±1.2	2.12±0.3	0.09±0.01	1.12±0.2	0.33±0.01	93.7±5.6
	72	9.03±0.8	62.0±4.0	2.73±0.1	1.94±0.2	14.8±1.5	2.43±0.3	0.11±0.01	1.42±0.1	0.60±0.03	94.4±6.2
	96	4.94±0.2	55.9±3.5	2.42±0.2	2.34±0.1	18.1±1.3	3.08±0.1	0.15±0.02	1.77±0.2	0.66±0.05	89.4±4.3
	144	3.92±0.3	48.7±4.7	1.94±0.2	2.40±0.3	23.5±1.5	4.03±0.2	0.30±0.02	2.48±0.3	0.86±0.1	88.1±6.1
	192	4.78±0.1	39.7±3.6	1.25±0.08	2.54±0.1	21.7±1.8	3.12±0.2	0.57±0.03	3.36±0.2	1.12±0.09	76.2±6.2
	240	4.12±0.2	32.5±2.9	0.94±0.1	2.34±0.2	16.6±1.6	2.56±0.1	0.80±0.05	3.74±0.5	1.40±0.2	64.3±4.5

**Table S10** The metabolites of OPE congeners identified by LC-Q-TOF-MS in the present study

Name	Structure <sup>a</sup>	Target Mass (m/z) <sup>b</sup>	Reaction	RT (min) <sup>c</sup>	Diff pos (ppm) <sup>d</sup>
TCEP-M1		555.0610	Glutathione S-addition (substitution of Cl)	2.26	4.56
TCEP-M2		265.9878	Oxidative dechlorination	4.87	-2.98
TCPP-M1		265.9878	Oxidative dealkylation Hydroxylation	1.89	-6.99
TCPP-M2		597.1080	Glutathione S-addition (substitution of Cl)	3.64	-2.24
TCPP-M3		308.0347	Oxidative dehalogenation	6.73 6.88	0.52
TCPP-M4		341.9957	Hydroxylation	8.42	1.03
TDCPP-M1		299.9488	Oxidative dealkylation dehalogenation	3.62 3.94	2.93
TDCPP-M2		698.991	Glutathione S-addition (substitution of Cl)	4.38	-5.64

TDCPP-M3		409.9178	Oxidative dehalogenation	7.52	-4.12
TPhP-M1		266.0344	Oxidative dealkylation hydroxylation	1.33	1.26
TPhP-M2		280.0501	Oxidative dealkylation hydroxylation methylation	1.86	-3.35
TPhP-M3		518.0952	Hydroxylation glucuronidation	4.31	-3.25
TPhP-M4		342.0657	Hydroxylation	6.47 6.80	0.21
TPhP-M5		358.0606	Hydroxylation	7.35 7.66	1.23
TPhP-M6		356.0814	Hydroxylation methylation	8.17	-0.74
TPhP-M7		534.0916	Hydroxylation glucuronidation	8.65	1.64
EHDPP-M1		266.0344	Oxidative dealkylation hydroxylation	2.67	0.87

EHDPP-M2		280.0501	Oxidative dealkylation hydroxylation methylation	4.52	-1.80
TnBP-M1		226.0970	Oxidative dealkylation hydroxylation	1.11	7.26
TnBP-M2		282.1596	Hydroxylation	2.43	7.99
TnBP-M3		298.1545	Hydroxylation	4.87 5.25	-2.63
TiBP-M1		154.0395	Oxidative dealkylation	1.57	0.37
TiBP-M2		226.0970	Oxidative dealkylation hydroxylation	3.29 3.41	5.17
TiBP-M3		282.1596	Hydroxylation	4.86 4.99	3.58
TiBP-M4		298.1545	Hydroxylation	5.22 5.51	-2.64
TBEP-M1		198.0657	Oxidative dealkylation (butoxyethyl)	1.04	6.44

TBEP-M2		242.0919	Oxidative dealkylations (butyl and butoxyethyl)	1.42	2.86
TBEP-M3		258.0868	Oxidative dealkylations (butyl and butoxyethyl) hydroxylation	1.64	8.55
TBEP-M4		314.1494	Oxidative dealkylation (butoxyethyl) hydroxylation	1.78 1.92	-5.83
TBEP-M5		358.1757	Oxidative dealkylation (butyl) hydroxylation	2.66 2.89	-1.23
TBEP-M6		342.1807	Oxidative dealkylation (butyl)	3.02	-4.66
TBEP-M7		414.2383	Hydroxylation	5.28 5.44	1.47
TBEP-M8		430.2332	Hydroxylation	7.79 7.90 8.21	2.75
TBEP-M9		518.2128	Oxidative dealkylation (butyl) glucuronidation	8.69	3.45

<sup>a</sup> The present structures are speculative because mass spectrum does not give information of the exact positions of the hydroxyl, methoxyl, glutathione, and glucuronide substituents.

<sup>b</sup> Exact molecular weight of OPE congener.

<sup>c</sup> Retention time.

<sup>d</sup> The deviation for observed mass at ESI negative mode.

**Table S11** Mass composition of OPEs, quantified metabolites, and semi-quantified products in plant exposure groups at the end of the experiment

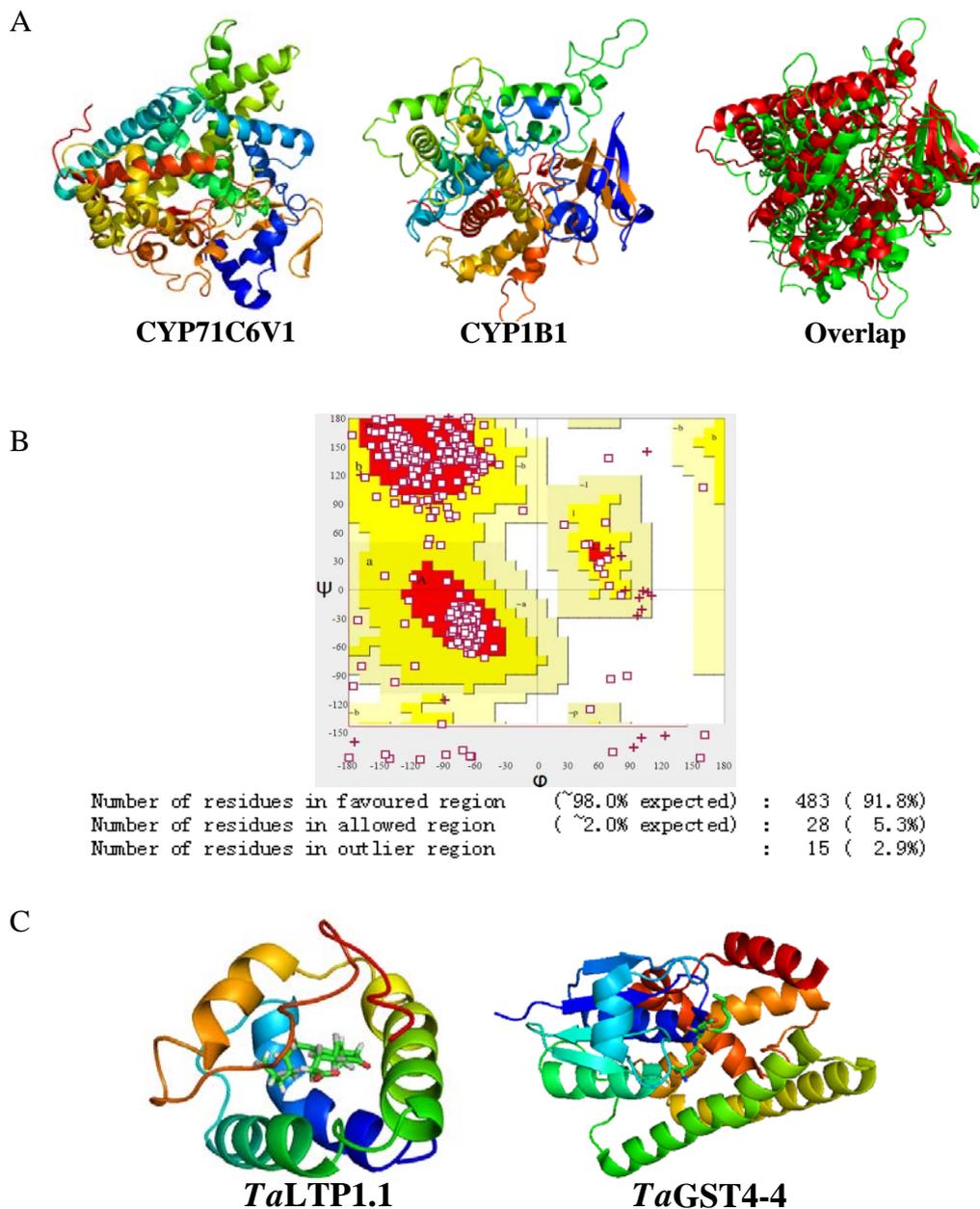
Compounds	Accumulation (%)		Quantified products (%)		Semi-quantified products(%)		Recovery(%)
	Solution	Plant	Solution	Plant	Solution	Plant	
TCEP	54.8±3.2	11.1±1.2	2.92±0.4	14.6±0.9	2.11±0.3	9.17±1.2	94.6±7.9
TCPP	45.8±3.5	10.7±0.7	2.31±0.3	11.7±1.2	3.75±0.3	12.3±1.4	86.5±7.2
TDCPP	34.3±3.3	13.0±1.1	4.14±0.2	19.5±1.5	2.56±0.3	7.76±1.1	81.1±5.6
TBEP	7.92±0.6	13.0±1.3	7.61±0.6	15.7±1.6	11.4±0.9	19.4±1.5	75.0±7.5
TiBP	15.1±2.0	8.14±0.5	6.73±0.7	16.3±2.0	7.14±0.8	17.8±1.3	71.1±6.8
TnBP	18.7±1.3	9.25±0.6	10.8±0.9	29.2±2.4	1.82±0.1	6.55±0.7	76.2±5.9
TPhP	10.6±0.9	30.6±2.5	2.52±0.1	15.8±1.3	2.11±0.1	15.5±1.0	77.1±7.8
EHDPP	5.41±0.2	33.4±3.2	3.51±0.4	27.1±2.9	1.51±0.2	9.49±1.2	80.3±6.7

**Table S12** Main interaction active site residues of *Ta*LTP1.1, *Ta*GST4-4 and CYP71C6v1

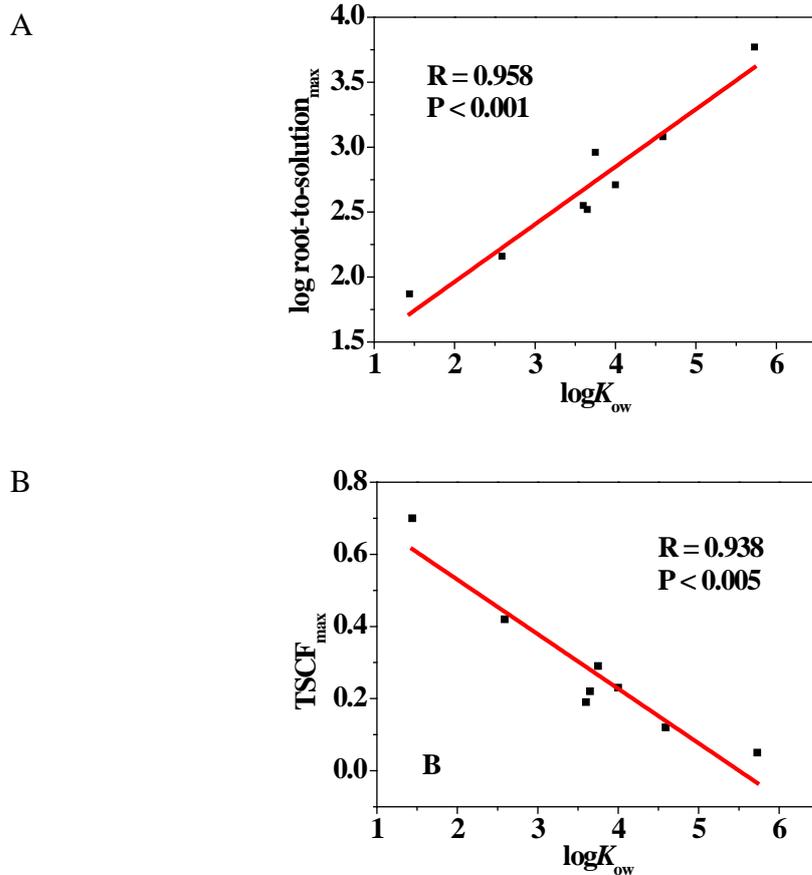
Compounds	Active site residues		
	<i>Ta</i> LTP1.1	CYP71C6v1	<i>Ta</i> GST4-4
TCEP	Val6, Leu34, Ala38, Ala47, Leu51, Leu77, Tyr79, Ile81	Ser78, Phe79, Leu187, Ala322, Glu325, Leu394, Arg466, Met506	Pro14, Ser15, Pro16, Phe17, Arg118, Trp171, Phe218
TCPP	Val6, Val10, Leu34, Ala38, Ala47, Leu51, Leu77, Thr80, Ile81	His76, Ser78, Phe79, Leu187, Ala322, Glu325, Leu394, Met506	Pro14, Ser15, Phe17, Ile56, Arg118, Phe218, Arg222
TDCPP	Val10, Val17, Cys27, Leu34, Ala47, Leu51, Ala66, Ile69, Ile81, Ser82	Ser78, Phe79, Leu187, Ala322, Glu325, Ala390, Leu394, Cys468, Met506	Pro14, Leu39, Lys55, Arg114, Arg118, Trp171, Arg222
TBEP	Val17, Val31, Leu34, Leu51, Ala55, Ile69, Leu77, Tyr79, Thr80, Ile81	His76, Ser78, Phe79, Leu187, Glu321, Ala322, Leu394, Met506	Pro14, Ser15, Leu39, Asn50, Lys50, Ile56, Arg114, Agr118, Arg222
TnBP	Val6, Leu34, His35, Ala38, Ala47, Leu77, Pro78, Tyr79, Ile81	His76, Ser78, Phe79, Leu187, Glu321, Ala322, Glu325, Met506	Ser15, Phe17, Lys55, Pro57, Arg114, Leu117, Trp171, Arg222
TiBP	Val10, Cys13, Leu14, Val17, Val31, Leu34, Val47, Tyr79, Ile81	Ser78, Phe79, Leu187, Asn318, Ala322, Leu393, Arg466, Met506	Pro14, Ser15, Pro16, Phe17, Leu39, Arg114, Arg118, Trp171, Arg222
TPhP	Leu34, Ala38, Cys50, Ile51, Leu77, Pro78, Tyr79, Ile81	His76, Ser78, Phe79, Leu187, Asn318, Glu321, Ala322, Glu325, Met506	Pro14, Ser15, Pro16, Phe17, Lys55, Arg118, Trp171, Phe218, Arg222
EHDPP	Val10, Val31, Leu34, Ala38, Ala47, Leu51, Leu77, Pro78, Tyr79, Ile81	Ser78, Phe79, Ala322, Ala390, Leu393, Phe461, Cys468, Ala469, Met506	Pro14, Phe17, Leu39, Lys55, Ile56, Arg114, Arg118, Trp171, Arg222

**Table S13** Binding affinities of OPE congeners with *TaLTP1.1*, *TaGST4-4* and *CYP71C6v1* (kcal/mol)

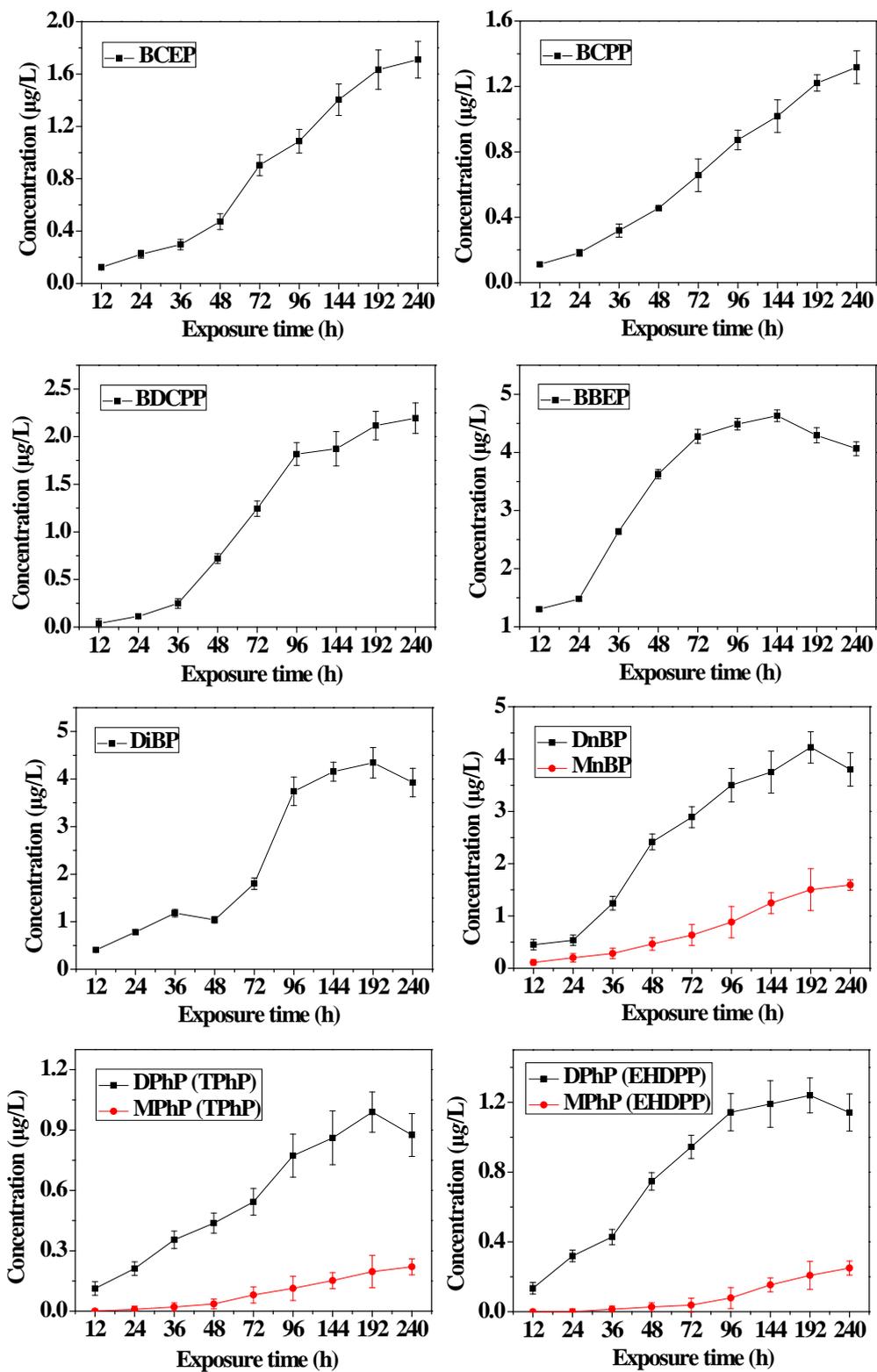
Compounds	Enzyme	Van der Waals energy	Electrostatic energy	Binding energy	Enzyme	Van der Waals energy	Electrostatic energy	Binding energy	Enzyme	Van der Waals energy	Electrostatic energy	Binding energy
TCEP	<i>TaLTP1.1</i>	-5.37	-0.01	-5.38	<i>CYP71C6v1</i>	-2.96	-0.06	-3.02	<i>TaGST4-4</i>	-4.73	-0.05	-4.78
TCPP		-5.95	0	-5.95		-3.85	-0.02	-3.87		-4.57	-0.06	-4.63
TDCPP		-6.46	-0.02	-6.48		-3.41	-0.02	-3.43		-4.44	-0.09	-4.53
TBEP		-7.08	0.05	-7.03		-9.30	0	-9.30		-6.68	0.03	-6.65
TnBP		-6.56	-0.01	-6.14		-5.56	0.15	-5.41		-4.99	-0.18	-5.17
TiBP		-6.16	0.02	-6.57		-5.26	-0.17	-5.43		-5.31	-0.01	-5.32
TPhP		-8.41	0	-8.41		-5.85	0.31	-5.54		-5.22	-0.18	-5.4
EHDPP		-8.09	-0.01	-8.10		-6.75	-0.07	-6.82		-5.99	-0.34	-6.33



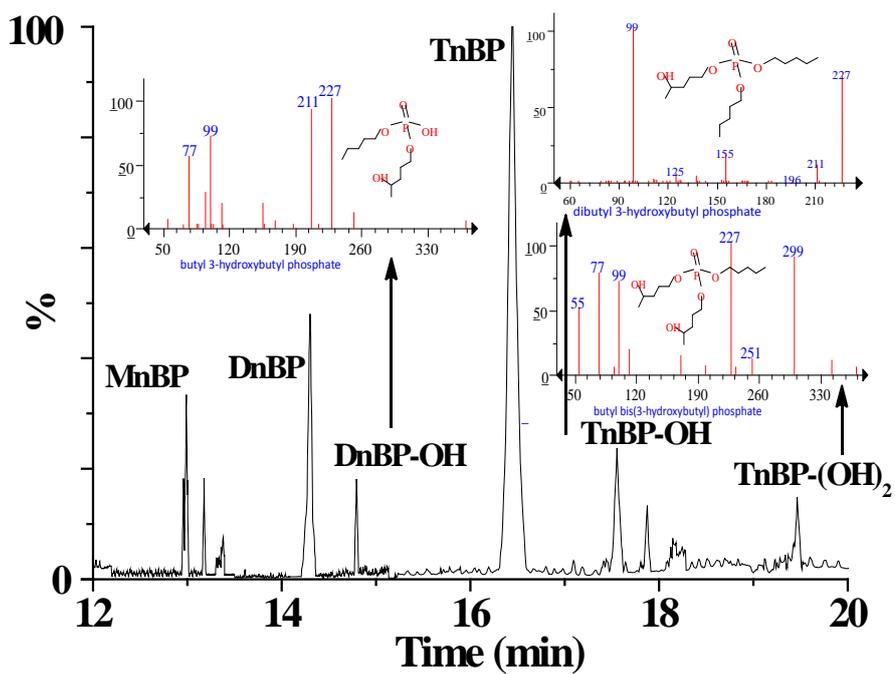
**Figure S1.** 3-D structures of CYP71C6v1 build by homology modeling (A) and evaluated by Ramachandran plot (B), and 3-D structures of *TaLTP1.1* and *TaGST4-4* (C). Human CYP450 1B1 (PDB ID: 3PM0, resolution: 2.70 Å) were employed as the templates for CYP71C6v1. The amino acid sequence identity was 25% for CYP71C6v1 to CYP1B1. The 3D models of CYP71C6v1 with all the structured regions labeled, shown by a cartoon representation of the structure colored using the rainbow gradient.



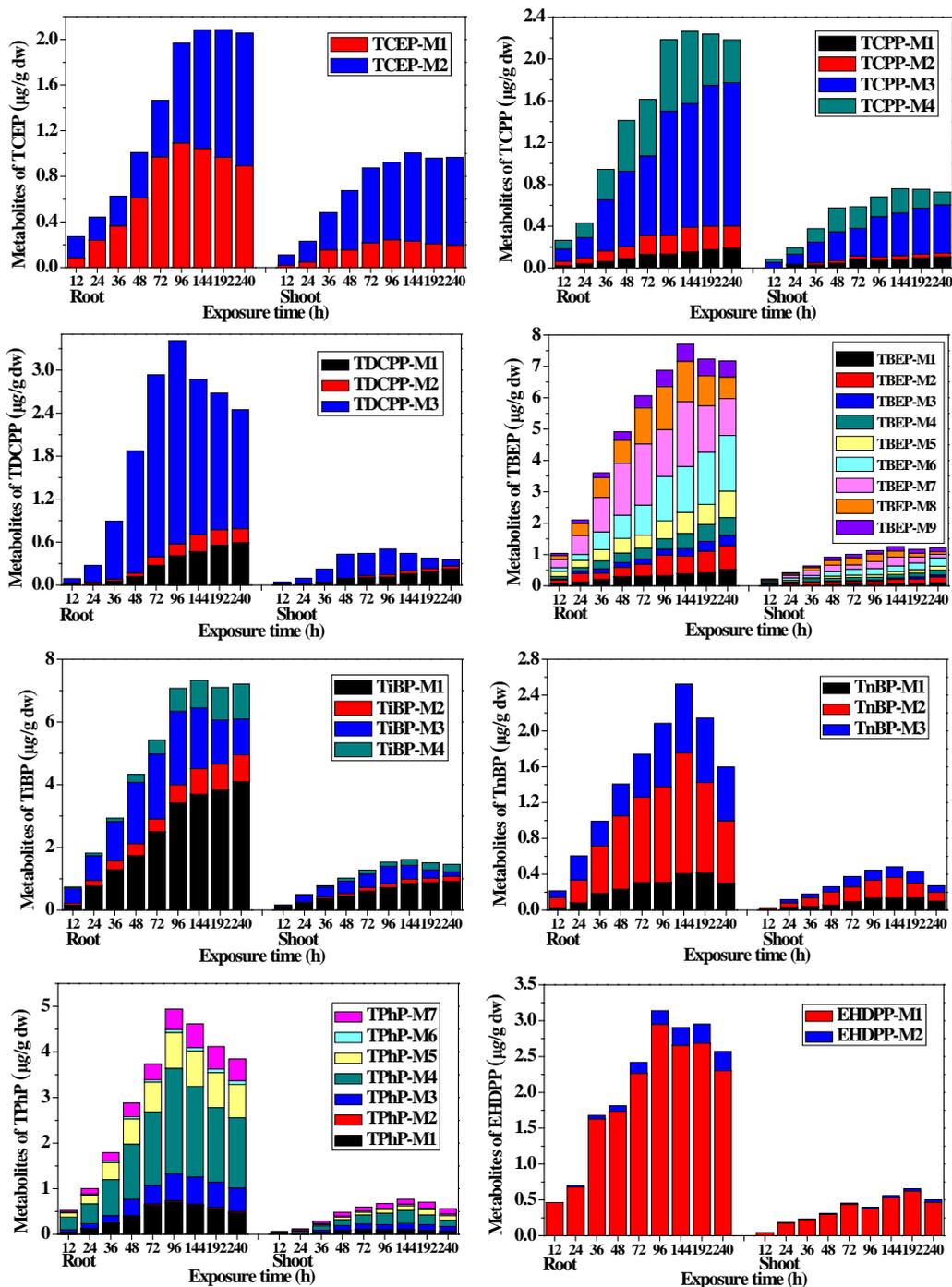
**Figure S2.** Relationships between the max log root-to-solution values and log $K_{ow}$  values (A), and between the max TSCF values and log $K_{ow}$  values (B) of OPEs in wheat plants.



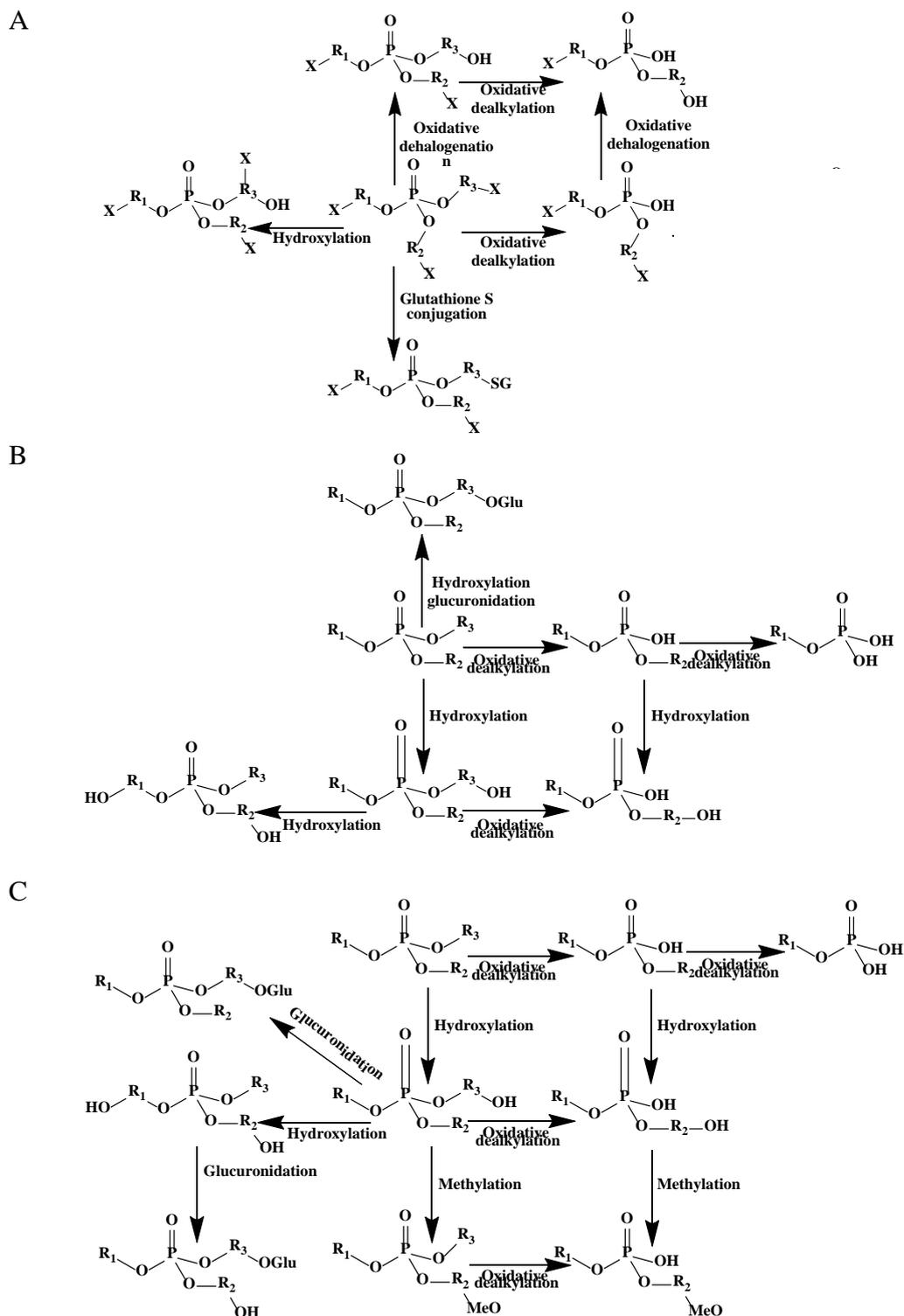
**Figure S3.** The concentrations of the quantified metabolic products in culture solutions of the plant exposure groups.



**Figure S4.** The gas chromatograms of OPEs under the scan mode with the identification of the metabolic products, taking TnBP as an example.

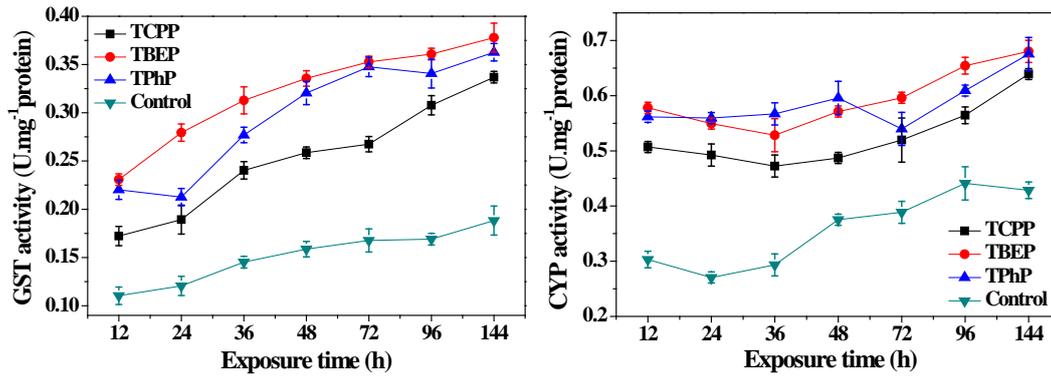


**Figure S5.** Time-dependent concentrations of the semi-quantified metabolites of OPE congeners in wheat tissues.

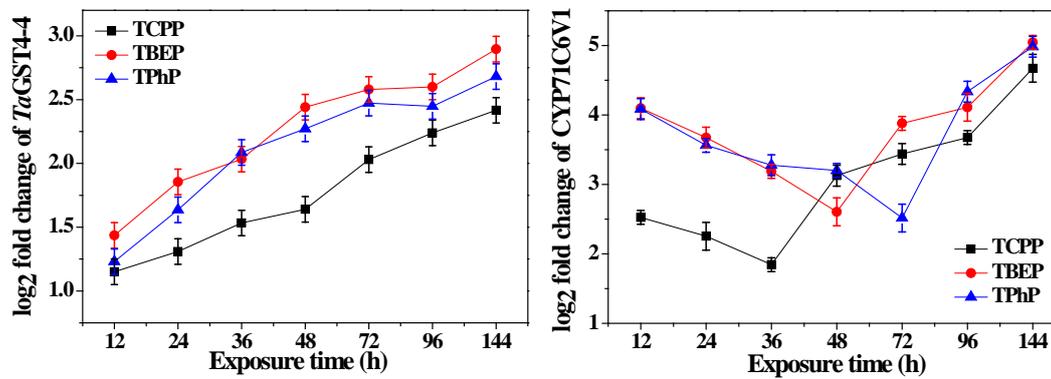


**Figure S6.** Biotransformation pathways of halogenated OPEs (A), non-halogenated aryl OPEs (B), and non-halogenated alkyl OPEs (C) in wheat tissues based on the metabolites detected by GC-MS and LC-Q-TOF-MS. R-X means haloalkane.

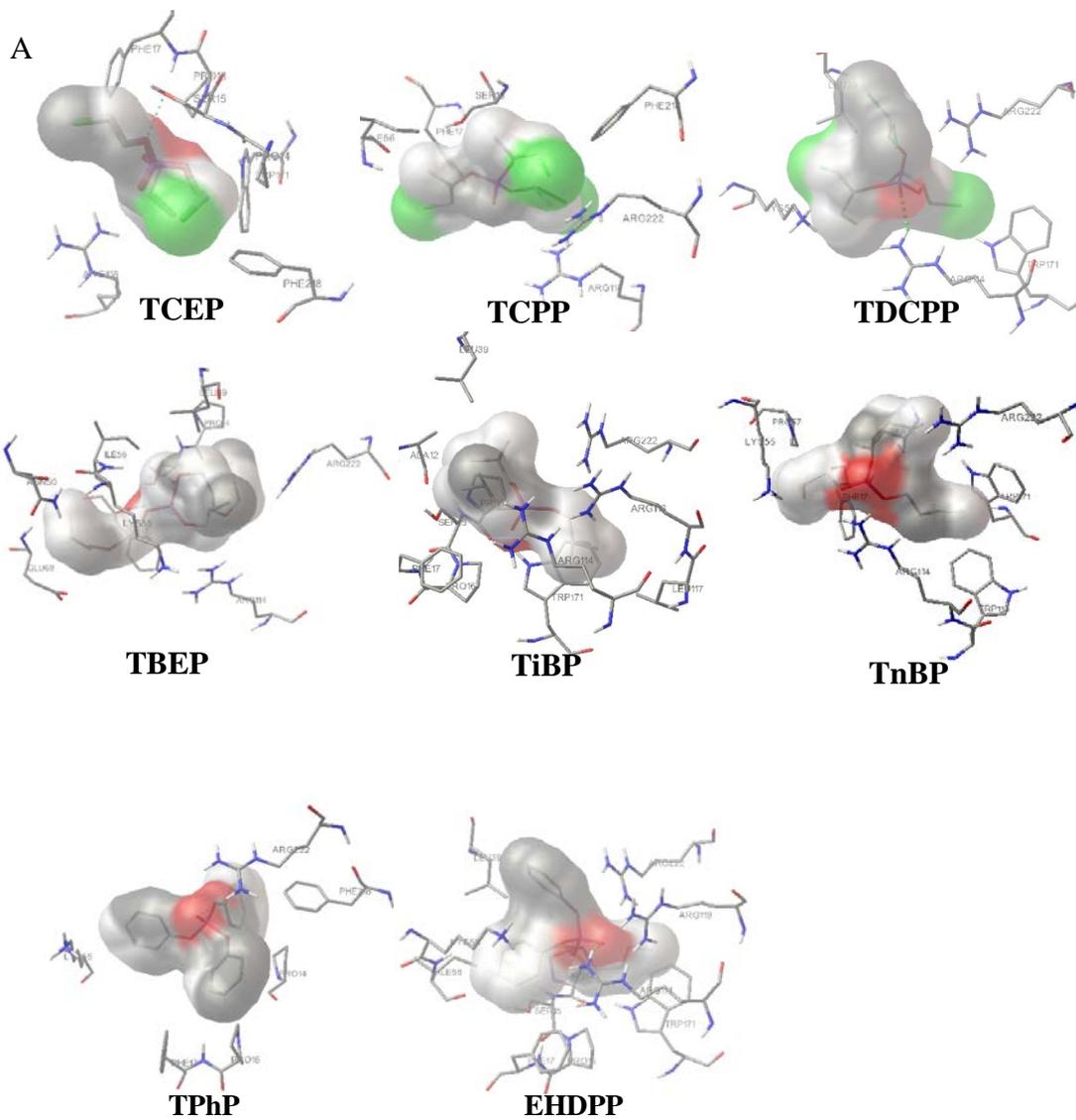
A



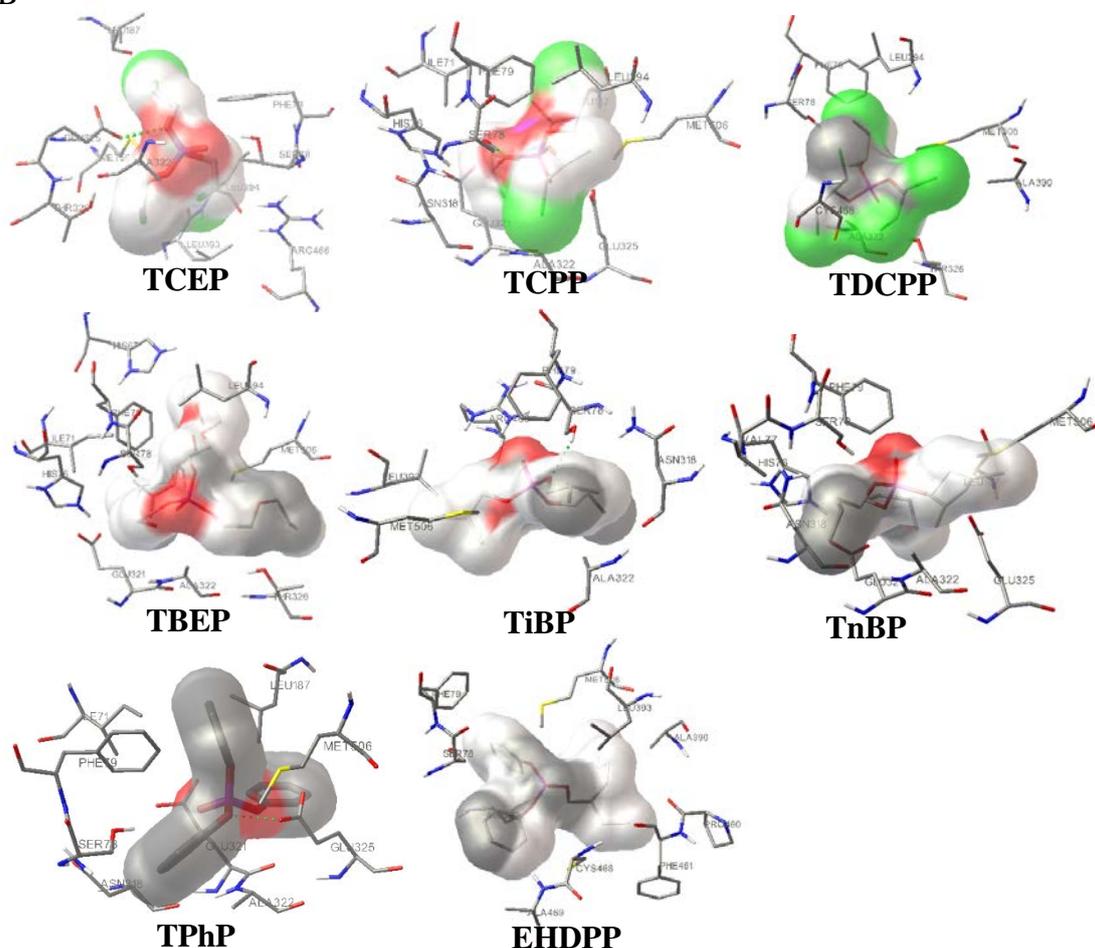
B



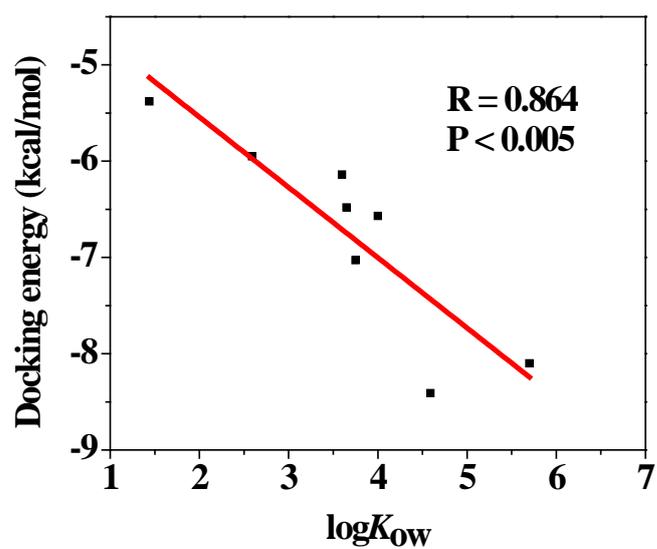
**Figure S7.** Dynamic changes of GST and CYP450 activities (A), and the qRT-PCR assays of gene expressions (B) in wheat roots during the exposure time taking TCPP, TBEP and TPhP as examples. There are significance differences in enzyme activities ( $P < 0.05$ ) between exposure groups and the blank control at the same time point. Activities of GST increased over the exposure time, and CPY450 activities decreased first and then increased from the exposure time of 36 h, which were 1.56–2.32, and 1.31–2.05 times as high as those of blank controls at each time point, respectively. Expressions of the *TaGST4-4* and *CYP71C6V1* genes were consistently up-regulated after exposure to OPEs. The fold change of *TaGST4-4* increased with increasing exposure time, and the fold change of *CYP71C6V1* decreased first and then increased at the exposure time of 36 h, 48h, and 72 h for TCPP, TBEP and TPhP, respectively.



B



**Figure S8.** Residues in the active sites of *TaGST4-4* (A) and *CYP71C6v1* (B) interacted with OPE congeners. Seven main residues including Pro14, Ser15, Phe17, Arg114, Arg118, Trp171, and Arg222, and six main residues including Ser78, Phe79, Leu187, Ala322, Glu325, and Met506, in the active sites belonged to *TaGST4-4* and *CYP71C6v1*, respectively, were found to be located in a distance within 3 Å to OPEs. The hydrogen bonds formed with the residues, including TCEP with Ser15, TDCPP and EHDPP with Arg114, and TPhP with Arg222 of *TaGST4-4*; and TCEP and TPhP with Glu325, TCPP and TiBP with Ser78 of *CYP71C6v1*, were displayed with green dotted lines.



**Figure S9.** Relationship between the docking energies and the logK<sub>ow</sub> values of OPEs congeners.

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