Supporting information

for

The fractions transformation and dissipation mechanism of Dechlorane Plus in the rhizosphere of soil-plant system

Yu Cheng†, Jue Ding‡, Xiuyu Liang§, Xiaowen Ji†, Ling Xu‖, Xianchuan Xie†‖, You-Kuan Zhang§*

†State Key Laboratory of Pollution Control and Resource Reuse, School of Earth Sciences and Engineering, School of the Environment, Nanjing University, Nanjing, P. R. China

‡ College of Environment, Hohai University, Nanjing, P. R. China

§ State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, Guangdong, P. R. China

‖ Nanjing Innovation Center for Environmental Protection Industry CO; Ltd., Nanjing, PR China

** Corresponding Author:*

Dr. Xianchuan Xie

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, P. R. China.

Nanjing Innovation Center for Environmental Protection Industry CO; Ltd., Nanjing, PR China.

Email: xchxie@nju.edu.cn & 24255542@qq.com

Tel & Fax: 086-25-83594492

Summary of supporting information :

Text S1. Materials and methods (**Page S1-5**)

Text S2. Derivation process for the model (**Page S6-14**)

Table S1. The parameters for the models (**Page S15**)

Table S2. The methodological detection limits (MDLs) and recoveries of the extraction methods used in the study (**Page S16**)

Table S3. Plant response on each sampling day during the long-term growth (**Page S17**)

Table S4. The concentration of DP in plant tissues and calculated translocation factor on each sampling day (**Page S18**)

Table S5. The residual concentrations of DP in each compartment on each sampling day (**Page S19-20**)

Table S6. DOC concentrations in each compartment of the rhizobox (**Page S21**)

Table S7. K values of fractions transformation of DP on the 150th day (**Page S22**)

Table S8. Respective contributions of microbial degradation, plant uptake, mobility and bound-residue formation to DP dissipation in soil (**Page S23**)

Table S9. The stereoselectivity of DP in plant tissues and DP fractions (**Page S24**)

Figure S1. The estimated coefficients in the model (**Page S25**)

Figure S2. The generation rate of DOC in soil with distance to roots (**Page S26**)

Figure S3. Relationship between the concentration of DP in rice roots and the concentration of labile DP in the root compartment (**Page S27**)

Figure S4. Simulation results of the plant uptake and residual DP concentrations (**Page**

S28)

Figure S5. Comparison of simulated and experimental data for the fractions of DP in the rhizosphere during cultivation (**Page S29**)

Text S1. Materials and methods.

S1.1 Chemicals and instruments. The Dechlorane Plus with a purity of 97% used in this study was purchased from J&K Scientific Ltd. DP stock solutions were prepared in acetone at 250 mg/L. Tenax-TA was obtained from Beijing KangLin Science & Technology Co. Ltd., China. All solvents were HPLC grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was self-manufactured using the Milli-Q Advantage A10 Ultrapure Water System in the laboratory. The samples were freeze-dried in a lyophilizer (FD-1, Biocool Instrument Ltd. Beijing).

S1.2 Preparation of DP spiked soils. The paddy soil used in this study was collected from the surface layer (0-10 cm) of a rice-grown area (31°93′ N, 119°07′ E) in Nanjing, China. The soil was air dried, gently crumbled and passed through a 2 mm sieve, discarding roots, other plant residues and fragments of organic matter. The soil was preliminarily analyzed for background signals to confirm no DP was detected. The soil consisted of 29.41% clay, 37.28% silt, 33.31% sand, and 2.51% organic matter, and had a pH of 6.7.

The soil was spiked with DP solutions (250 mg/L in acetone) to prepare S1 (100 ng/g), S2 (1000 ng/g), and S3 (10000 ng/g) soils based on environmental DP levels. After evaporation of acetone, the soil was thoroughly mixed and homogenized. Portions (80 g in the root compartment and 40 g in each outer compartment) of the soils were packed uniformly into the rhizobox, giving a bulk density of 1.25 g/cm^3. The upper 0.5 cm of each rhizobox was covered with fine sand to avoid the atmospheric DP deposition, water loss and evaporation of DP from soil.

S1.3 Rice cultivation. Rice seeds (*Oryza sativa* L. cv. Yiyou 1988) were purchased from the Nanjing Institute of Agricultural Sciences, Nanjing, China. The seeds were sterilized in 10% (w/w) H_2O_2 solution for 30 min, thoroughly washed by deionized water, soaked in the deionized water in the dark for 12 h, and germinated on moist gauze in the dark. Ten pregerminated seeds were transplanted in the root compartment and 3 days after emergence 3 seedlings with vigorous and uniform growth were left. Nonspiked soil with rice growing was additionally carried out as the DP-free blank control. The rhizoboxes were placed randomly side-by-side and relocated every five days in a greenhouse at a 32/22 ℃ day/night temperature regime and a relative humidity of about 60%. Halide lamps were used as supplementary illumination to provide a light intensity of 800 μmol $m^{-2}s^{-1}$ for a photoperiod of 12h at daytime. To avoid the infiltration of DP caused by irragation from top, the soil was connected to a water reservoir containing nutrient solution below the rhizobox via fiberglass filter paper wicks and the length of the wicks was adjusted to keep the moisture at 48% by weight. The solution in the reservoir was prepared based on that of Yoshida and refreshed twice monthly.

S1.4 Sample preparation. The growth was sustained for 150 days and every 15 days after transplanting the rhizoboxes were detached. Plant shoots were divided into stems and leaves and were separately sampled with roots, and rice grains were harvested on the 150th day. The root, shoot and grain samples were rinsed with water, freeze-dried, weighed to determine dry weights, ground separately, and then thoroughly mixed respectively. The fine sand on the top was removed and the soil sample in each

compartment was collected, freeze-dried and homogenized to assess soil properties, e.g., pH, soil organic carbon (SOC), microbial biomass carbon (MBC).

S1.5 Extraction of Dissolved organic carbon (DOC). One day before the plant sampling, soil water samplers were installed in every compartment, connected to glass syringes, and set to a suction of 400 hPa to collect 2 ml soil water. Then water sample was analyzed for DOC content by a TOC analyzer (Acquray series, Elementar, Germany).

S1.6 Extraction and Analysis of DP. Triplicates of a 1 g aliquot of soil (dry weight) in each compartment of rhizobox were subjected to sequential extraction. The labile, stable-adsorbed, and bound-residue fractions of DP in soils were sequentially treated by Tenax-TA, the mixtures of hexane and acetone with UAE, and alkaline hydrolysis in a water bath, respectively.

For the labile fraction, Tenax-TA beads (0.5 g) were added only once, separated after 10 h of shaking, rinsed, and extracted by UAE with 3 × 10 mL of hexane:acetone solvents (1:1, v/v) for 10 min. The combined extracts were passed through a 0.22-μm filter membrane and concentrated to 1 mL for analysis.

For the stable-adsorbed fraction, soil samples which has been extracted by Tenax-TA were lyophilized and then extracted 3 times with 10 mL of hexane:acetone (1:1 v/v) with UAE method. After centrifugation, the combined extracts were collected, passed through a 0.22-μm filter membrane, and then concentrated to 1 mL for gas chromatography/mass spectrometry (GC-MS) analysis.

For the bound-residue fraction, the remaining soil previously extracted by the UAE

method was then poured into to a 10-mL Teflon centrifuge tube to which 2 mL of 1 N NaOH solution was added, followed by 8 h of water-bath heating at 80°C. After cooling, the mixtures were lyophilized and then extracted by UAE using 3 × 5 mL of hexane:acetone (1:1, v/v) for 10 min. Following centrifugation, the extracts were combined, passed through a 0.22-μm filter membrane, and then concentrated to 1 mL for analysis.

Analysis of DP was performed with GC-MS (a Thermo DSQ II system) operating in the electron capture negative ionization (ECNI) mode. ECNI-selected ion monitoring was used for measurement, and ions of 651.5 and 653.5 m/z were monitored for syn- and anti-DP. Then, 1 μL of the extract sample was injected into the gas chromatograph in splitless mode. The injection port and transfer line were held at 275°C. The ion source temperature was 280°C. Helium was used as the carrier gas at a flow rate of 1.0 mL/min, and the reagent gas was methane. The separation used a 30-m HP-5MS capillary column (0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies, Inc.). The GC oven temperature program started at 100°C for 1 min, then increased by 10°C/min to 280°C, which was held for 2 min, and then increased by 5°C/min to 300°C, which was held for 10 min.

S1.7 Soil pH analysis. The soil pH was measured with a glass electrode (PHSJ-6L pH analyzer, Lei-ci, China) in samples with a soil:water ratio of 1:2.5.

S1.8 Soil organic carbon (SOC). The SOC concentration was used to determine soil organic matter (SOM) content in each compartment, using the dichromate oxidation method, which means the oxidation of organic matter by a mixture of H_2SO_4 and

$K_2Cr_2O_7$ with titration of $FeSO_4 \cdot 2SO_4 \cdot 6H_2O$ [1].

S1.9 MBC analysis. In brief, the fumigated and nonfumigated soils were extracted by 0.05 mol/L K_2SO_4 solution (w:v=1:4). The contents of organic carbon in the extracts were measured with a multi N/C analyzer (multi N/C analyzer 3100, Analytik Jena, Germany). MBC was calculated by equation:

$$\mathrm{MBC} = \frac{C_{fumigation} - C_{unfumigation}}{K_{EC}}$$

where $C_{fumigation}$ and $C_{unfumigation}$ were the concentrations of dissolved organic C (g/kg soil) in the extracts of fumigated and non-fumigated soils, respectively; KEC=0.45 [2].

Text S2. Derivation process for the model.

S2.1 Plant uptake and depuration

Plants accumulate organics through passive root uptake of organics dissolved in water, which could be represented by the flow of organics into roots associated with flow of water supplying the plant transpiration demand [3]. The magnitude of potential root water uptake rate is defined as s_p, corresponding to the potential transpiration rate, T_p. The root water uptake is distributed over the root zone according to the root distribution in the root compartment. The potential transpiration is determined by the atmospheric demand controlled by meteorological variables, such as solar radiation, temperature, wind speed, and relative humidity.

When distributing the potential water uptake rate equally over a two-dimensional rectangular root domain, s_p becomes:

$$s_p(t) = \beta(t)\gamma T_p(t) \quad \text{(Sq1)}$$

where s_p is the potential root water uptake rate [day^{-1}] at time t, T_p is the potential transpiration rate [cm day^{-1}], $\beta(t)$ is the normalized water uptake distribution function [cm^{-2}], γ is the stress response function, which is a prescribed dimensionless function of the soil water and osmotic pressure heads discussed in extensive literatures [4-6].

The normalized water uptake distribution $\beta(t)$ is a function of space and time, allowing for plant root growth, and must be normalized to ensure $\beta(t)$ integrates to unity over the flow domain, i.e.:

$$\int_{\Omega R} \beta(t) dR = 1 \quad \text{(Sq2)}$$

and

$$\beta(t) = \frac{R(z)}{\int_{\Omega R} R(z)dz} \quad \text{(Sq3)}$$

where ΩR represents the root zone [cm^2], R(z) represents the various root length density at depth Z [cm]. Rice roots in the root compartment could be considered as uniform distribution during cultivation, and thus the equation could be simplified as:

$$\beta(t) = \frac{R(z)}{\int_{\Omega R} R(z)dz} = \frac{R(z)}{R(z) * S_R(t)} = \frac{1}{S_R(t)} \quad \text{(Sq4)}$$

where $S_R(t)$ represents the area of the root zone [cm^2].

In the present study, water supply for the rice growth was continually adjusted by the fiberglass filter paper wicks which were connected to a water reservoir. Therefore, there is no stress response in the root compartment during cultivation, that is γ=1. Additionally, the growing conditions, such as solar radiation, temperature, wind speed, and relative humidity, which could control the potential transpiration, were regulated during cultivation. Therefore, the potential transpiration rate, $T_p(t)$ [cm day^{-1}], is defined as:

$$T_p(t) = T_{pm}\frac{m_{lf}(t)}{M_{lf}} \quad \text{(Sq5)}$$

where T_{pm} represents the maximum potential transpiration rate of plants, which is approximately averaged as 0.1 cm/day in the present study on the 105th day. $m_{lf}(t)$ [g] represents the total mass of leaves on t days, and M_{lf} [g] is determined as the maximum total mass of leaves by experimental observation on the 105th day in the present study. It is known that the dissolved fraction of DP in water could be accessible to soil organisms, that is rice roots uptake the dissolved DP in the water flow. Therefore, passive DP uptake is simulated by multiplying root water uptake with the dissolved DP concentrations in the present study, which is described as:

$$p_a(t) = s_p(t) * L_w(t) \quad \text{(Sq6)}$$

where p_a [ng $cm^{-3}day^{-1}$] represents the mass of DP removed per unit time from a unit volume of soil due to passive plant water uptake, $L_w(t)$ [ng cm^{-3}] represents the dissolved DP concentration in soil water that can be taken up by roots during passive root uptake.

The rate of DP uptake by roots α can be calculated as:

$$\alpha = s_p(t)/\theta \quad \text{(Sq7)}$$

where θ represents the water content of soil in rhizoboxes.

Intuitively, the accumulated DP in plants can be calculated by an equation of

$$\frac{dC}{dt} = \frac{p_a(t) \times V_R}{m(t)} - k_{pl}C \quad \text{(Sq8)}$$

where C is the concentration of DP in plants [ng/g], m(t) [g] is the total mass of rice plant in one rhizobox at time t [day], V_R is the volume of the root compartment where roots uptake DP [cm^3], and k_{pl} represents the depuration rate of DP in plants [day^{-1}]. This model was well fitted with R^2 = 0.966 (**Figure S4a**), and the parameter was calibrated as k_{pl} = 0.016 (**Table S8**).

S2.2 Root-induced DP transport

S2.2.1 The calculation of DP in rhizosphere.

The dissolved fraction is an indispensable part of the labile fraction, which dissolves and diffuses in soil water (L_w) and reversibly equilibrates with the rapidly dissolved fraction adsorbed on soil (L_s). L_w could transfer in soil water and L_s participates in the fractions transformation, that is:

$$DP = L + S + B \quad \text{(Sq9)}$$

$$L = L_w + L_s \quad \text{(Sq10)}$$

$$DP_s = L_s + S + B \quad \text{(Sq11)}$$

$$DP = L_w + DP_s \quad \text{(Sq12)}$$

where L, S, and B represent the concentration of the labile, stable-adsorbed, and bound-residue fractions of DP in soil, respectively. L_w, L_s, and DP_s are concentrations of dissolved fraction of DP in soil water, labile fraction adsorbed in the soil-water interface, and total DP adsorbed on soil particles, respectively. Therefore, the transport of DP in the rhizosphere could be described as:

$$\frac{\partial DP}{\partial t} = \frac{\partial(\theta L_w)}{\partial t} + \frac{\partial(\rho DP_s)}{\partial t} = D_w \theta f \partial^2 L_w / \partial x^2 - \theta k_{DP} L_w \quad \text{(Sq13)}$$

where ρ is the soil density, θ is the water content, D_w is the diffusion coefficient of DP in soil water, f is diffusion impedance factor, k_{DP} is the first order degradation rate constant for dissolved fraction of DP in soil.

Through chain rule:

$$\frac{\partial DP_s}{\partial t} = \frac{\partial DP_s \partial L_w}{\partial L_w \ \partial t} \quad \text{(Sq14)}$$

and

$$\frac{\partial L}{\partial t} = \left(1 + \frac{\rho \partial L_s}{\theta \partial L_w}\right) \frac{\partial(\theta L_w)}{\partial t} \quad \text{(Sq15)}$$

According to the definition of buffering factor [1]:

$$b_w = 1 + \frac{\rho \partial L_s}{\theta \partial L_w} \quad \text{(Sq16)}$$

Therefore Eq. (Sq13) could be transformed as:

$$b_w \frac{\partial(\theta L_w)}{\partial t} = D_w f \frac{\partial^2(\theta L_w)}{\partial x^2} - \theta k_{DP} L_w \quad \text{(Sq17)}$$

S2.2.2 DOC in rhizosphere.

Considering the diffusion and root-induced generation of DOC away from the root compartment, and the decomposition of DOC in soil water follows first-order kinetics, then the rhizosphere effect on spatial variation of DOC content could be expressed as Eq. (Sq18):

$$b_{DOC}\frac{\partial(\theta M)}{\partial t} = D_{DOC}f\frac{\partial^2(\theta M)}{\partial x^2} + \theta\sigma(x) - k_{DOC}\theta M \quad \text{(Sq18)}$$

where b_{DOC} is the soil buffer power for DOC, M is the concentration of DOC in soil water, D_{DOC} is the diffusion coefficient in soil water, k_{DOC} is the first order rate constant for DOC decomposition. $\sigma(x)$ is the root-induced generation rate of DOC in the distance of x [mm] away from the roots [mg/ (L·day)].

According to Kirk (1999), the value of b_{DOC} is approximately 5.8 and f is 0.40 in this study. And θ is 0.48 in this study.

$\sigma(x)$ could be described as:

$$\sigma(x) = a_1 \exp\left(\frac{a_2}{x^2 + a_3}\right) \quad \text{(Sq19)}$$

In this study, the DOC equation was calibrated using the data of DOM in the experiments. With R^2 =0.810, the equation was well fitted, and the parameters were calibrated as D_{DOC} = 0.0069, k_{DOC} = 0.01, a_1 = 68.46, a_2 = 2.69, a_3 = -1.19.

Therefore, $\sigma(x)$ can be shown in **Figure S2**. It is noted that the generation rate of DOC (σ) decreased with distance to roots and could be neglectable from the 8 mm compartment. The limited excitation extent could be explained by the slow diffusion and rapid microbial decomposition of root exudates, leading to DOC gradients in the rhizosphere.

S2.2.3 Calculated solubilization of DP by DOC.

In the rhizosphere, the solubility of DP in soil water can be facilitated by root-

induced DOC changes. Therefore, the solubilization effect of DP by DOC in the transport process should be taken into consideration. Based on the theory for the diffusion of two interacting solutes in soil, the modified transport of DP in the rhizosphere can be described by the following diffusion equation:

$$b_w\theta\frac{\partial(L_w - \lambda M)}{\partial t} = D_w\theta f\partial^2 L_w/\partial x^2 - \theta k_{DP} L_w \quad \text{(Sq20)}$$

where λ is introduced as a DP-DOC interaction coefficient in the rhizosphere. According to Nye (1984):

$$(-\Delta DP/\Delta M)_{[L_w]} = \lambda b_w/b_M \quad \text{(Sq21)}$$

The value of b_w could be estimated from the sorption curve of DP on soil (**Figure S1a**) which also obeys the Freundlich adsorption isotherm (**Figure S1b**), and $b_w = \frac{dL_s}{dL_w} \approx 220$.

The quantity of $(-\Delta DP/\Delta M)_{[L_w]}$ can be estimated from the data of DP and DOM concentrations in the rhizosphere (**Figure S1c**) to be 0.0004. Therefore, the value of λ is 1.09×10^{-5} in this study.

This model was well fitted with R^2 >0.820 (**Figure S4b**), and the parameters were calibrated as $D_w = 8 \times 10^{-6}$, and k_{dp} were 0.32~0.19 d^{-1} from rhizosphere to nonrhizosphere.

S2.3 Fractions transformation

The equations describe fractions transformation of DP in the rhizosphere are modified based on our previous study：

$$\frac{dL_s}{dt} = -k^1 L_s - k^3 L_s + k^2 S + k^4 B + \frac{\partial DP}{\partial t} \quad \text{(Sq22)}$$

$$\frac{dS}{dt} = -k^2 S - k^5 S + k^1 L_s + k^6 B \quad \text{(Sq23)}$$

$$\frac{dB}{dt} = - k^4B - k^6B + k^3L_s + k^5S \quad \text{(Sq24)}$$

where L_s, S, B represent the concentrations of labile, stable-adsorbed, and bound-residue DP in soil, respectively [ng/g]; K_i (i=1,2, …, 6) represents the rate coefficient for transformation of DP between different fractions (day^{-1}). $\frac{\partial DP}{\partial t} = b_w\theta\frac{\partial(L_w - \lambda M)}{\partial t}$ is the variation of total DP concentrations in soil phase, which is affected by the other two models above.

This model was well fitted with R^2 >0.750 (**Figure S5**). The parameters K1~K6 were calibrated in **Table S7**.

S2.4 The initial conditions and boundary conditions

The initial condition of plant uptake and depuration model (**S2.1**):

$$C = 0 \qquad t = 0 \quad \text{(Sq25)}$$

The initial condition of root-induced DP transport (**S2.2**) is calculated using the Freundlich adsorption isotherm (**Figure S2b**):

$$L_w = C_e \qquad q_e = 100, 1000, 10000\ ng/g \quad \text{(Sq26)}$$

The initial conditions of fractions transformation (**S2.3**) is determined by the experimental data on day 0.

The rhizosphere boundary condition is:

$$\frac{D_w\theta f dL_w}{dx} = -\alpha L_p \qquad \text{x} = 0 \text{ mm}, t \geq 0 \quad \text{(Sq27)}$$

where α is the root absorbing power for solute. Based on the passive root uptake theory, α can be determined as:

$$\alpha = s_p(t)/\theta \quad \text{(Sq28)}$$

where s_p(t) represents the potential root water uptake rate for rice plants, day^{-1}.

At the outer boundary (x = 10 mm), there will be no diffusion of DP and DOC.

Therefore,

$$\frac{D_w \theta f dL_w}{dx} = 0 \quad \text{x} = 10 \text{ mm}, t \geq 0 \tag{Sq29}$$

$$\frac{D_{DOC} \theta f dM}{dx} = 0 \quad \text{x} = 10 \text{ mm}, t \geq 0 \tag{Sq30}$$

S2.5 Total dissipation calculation.

The total dissipation (TDP) is the percentage of dissipative amount of DP caused by rhizosphere effects [%]. TDP at x [mm] away from the roots were calculated as the sum of four aspects, that is the plant uptake (F_{uptake}), modified diffusion ($F_{diffusion}$), microbial degradation ($F_{degradation}$), and bound-residue formation (F_{bound}):

$$\text{TDP} = F_{uptake} + F_{diffusion} + F_{degradation} + F_{bound} \tag{Sq31}$$

where F_{uptake}, $F_{diffusion}$, $F_{degradation}$, and F_{bound} are the dissipative percentage of DP caused by each aspect [%] within cultivation time.

And within cultivation time from t_1 to t_2, each aspect can be calculated as:

$$F_{mobility} = \int_{t1}^{t2} D_w f \frac{\partial^2(\theta L_w)}{\partial x^2} dt \tag{Sq32}$$

$$F_{degradation} = \int_{t1}^{t2} -\theta k_{DP} L_w dt \tag{Sq33}$$

$$F_{uptake} = \int_{t1}^{t2} -\alpha L_w dt \tag{Sq34}$$

$$F_{bound} = \int_{t1}^{t2} (-k_4 B - k_6 B + k_3 L + k_5 S) dt \tag{Sq35}$$

Therefore, the respective contributions [%] of the excitation effect and aging effect to the total dissipation are:

$$\text{Exitation} = \frac{F_{diffusion} + F_{degradation} + F_{uptake}}{\text{TDP}} \tag{Sq36}$$

$$\text{Aging} = \frac{F_{bound}}{\text{TDP}} \tag{Sq37}$$

S2.6 Calculation method and parameter determination

The models are solved using the finite difference method. The parameters of the models are determined using empirical values, experimental data and model calibration where genetic algorithm is applied in **Table S1**.

[1] Nelson, D. W. Total carbon, organic carbon and organic matter. Methods of Soil Analysis, 1982, 9, 961-1010.

[2] Xiaoting, Wang.; Ruirui, Chen.; Zhongwang, Jing.; Tongyan, Yao.; Youzhi, Feng.; Xiangui, Lin. Root derived carbon transport extends the rhizosphere of rice compared to wheat. Soil Biology & Biochemistry. 2018, 122, 211-219.

[3] Jirí, Simunek.; Jan, W. Hopmans. Modeling compensated root water and nutrient uptake. Ecological modeling. 2009, 220, 505–521.

[4] Cardon, G.E., Letey, J., 1992. Plant water uptake terms evaluated for soil water and solute movement models. Soil Sci. Soc. Am. J. 32, 1876–1880.

[5] Feddes, R.A., Raats, P.A.C., 2004. Parameterizing the soil–water–plant root system. In: Feddes, R.A., de Rooij, G.H., van Dam, J.C. (Eds.), Proceedings of the Unsaturated Zone Modelling: Progress, Challenges and Applications.

[6] Skaggs, T.H., Van Genuchten, M.Th., Shouse, P.J., Poss, J.A., 2006. Macroscopic approaches to root water uptake as a function of water and salinity stress. Agric. Water Manag. 86, 140–149.

Table S1. The parameters for the models.

Plant uptake and depuration	
γ°	1
T_{pm}°	0.1 cm/day
k_{pl}*	0.016 d^{-1}
Root-induced DP transport	
ρ°	1.25 g/cm3
θ°	0.48
$F^{\#}$	0.4
λ°	1.09×10^{-5}
b_w°	220
b_{DOC}°	5.8
D_w*	8×10^{-6}
D_{DOC}*	0.0069
k_{DP}*	0.19~0.32 d^{-1}
k_{DOC}*	0.01 d^{-1}
Fractions transformation	
K_1-K_7*	Table S7

Note: ° represents the parameter is determined by experiments; # represents the parameter is determined by empirical value; * represents the parameter is determined by model calibration.

Table S2. The methodological detection limits (MDLs) and recoveries of the extraction methods used in the study.

Extraction of DP	MDLs (ng/g)	Recovery (%)
Tenax extraction for labile DP	0.013±0.001 ~ 0.032±0.002	86.5±7.1 ~ 92.3±8.9
UAE for stable-adsorbed DP	0.006.0±0.001 ~ 0.019±0.002	92.1±9.3 ~ 96.2±7.2
Alkaline-Hydrolysis for bound-residue DP	0.023±0.002 ~ 0.045±0.003	80.2±6.5 ~ 87.5±9.3
DP in rice roots	0.047±0.005 ~ 0.072±0.005	82.3±5.6 ~ 86.9±8.7
DP in rice shoots	0.052±0.004 ~ 0.076±0.006	76.8±7.1 ~ 82.1±9.2

Data are means of three replicates.

Table S3. Plant response on each sampling day during the long-term growth for 150 days in the S1, S2, and S3 soils, including heights (cm) and biomasses of roots, shoots, and leaves (g plant^{-1}, DW). In addition, setting rates (%), the ratio of blighted grain to total grain amounts, were calculated on the harvest day.

soil	Plant tissues	cultivation time (day)									
		15	30	45	60	75	90	105	120	135	150
control	root (g)	0.32±0.05	0.98±0.01	2.27±0.21	3.06±0.33	3.22±0.19	3.70±0.37	4.13±0.38	3.79±0.28	3.72±0.31	3.51±0.33
	shoot (g)	0.62±0.05	2.21±0.29	5.39±0.39	10.27±1.24	14.52±0.88	25.13±1.59	38.52±3.12	47.32±4.33	53.87±5.15	61.97±5.69
	leaf (g)	-	-	2.52±0.22	4.73±0.51	6.22±0.47	8.92±0.63	9.98±6.64	11.76±0.88	12.13±1.09	13.62±1.35
	height (cm)	8.3±0.7	13.6±1.24	48.2±0.57	71.2±5.2	84.1±6.6	93.2±7.3	98.6±6.2	103.1±7.1	104.9±5.1	106.8±6.9
	setting rate										79.7±5.2%
S1	root (g)	0.32±0.02	0.92±0.07	2.29±0.31	3.02±0.31	3.26±0.42	3.62±0.21	4.04±0.39	3.73±0.22	3.71±0.34	3.52±0.39
	shoot (g)	0.63±0.03	2.19±0.35	5.52±0.48	10.46±0.92	14.71±1.39	24.95±2.64	38.12±2.95	46.83±5.13	54.73±4.79	62.23±4.89
	leaf (g)	-	-	2.53±0.22	4.78±0.38	6.39±0.52	8.60±0.63	10.07±0.82	11.23±1.12	11.88±1.07	12.47±1.15
	height (cm)	8.2±0.6	13.1±1.1	47.6±2.97	70.5±4.4	83.7±6.2	93.5±4.7	97.7±5.9	101.5±6.7	104.9±7.5	107.4±8.2
	setting rate										82.5±5.6%
S2	root (g)	0.33±0.04	1.02±0.15	2.24±0.21	2.92±0.23	3.13±0.32	3.84±0.32	4.11±0.32	3.85±0.19	3.68±0.29	3.43±0.36
	shoot (g)	0.61±0.05	2.24±0.31	5.36±0.32	10.32±1.11	14.17±1.52	25.33±2.72	38.18±0.29	47.52±3.35	52.57±5.15	62.35±4.69
	leaf (g)	-	-	2.46±0.31	4.62±0.52	5.96±0.49	9.12±0.71	10.11±1.21	11.43±0.82	11.56±1.03	12.47±0.95
	height (cm)	8.1±0.5	13.4±1.1	48.8±0.53	72.2±6.4	82.5±4.2	92.8±7.2	97.4±6.6	102.2±5.9	103.3±5.3	106.9±6.9
	setting rate										81.2±6.3%
S3	root (g)	0.39±0.04	1.16±0.13	2.44±0.19	3.13±0.24	3.64±0.27	4.05±0.32	4.56±0.29	4.15±0.41	3.91±0.36	3.82±0.28
	shoot (g)	0.59±0.03	2.26±0.19	5.37±0.43	9.96±0.63	13.17±1.15	24.21±1.83	37.83±4.12	47.52±4.23	51.75±3.95	61.13±6.33
	leaf (g)	-	-	2.49±0.21	4.83±0.29	6.18±0.63	8.71±0.57	10.05±0.99	12.13±1.17	12.83±1.08	14.75±1.14
	height (cm)	8.3±0.04	13.9±0.92	49.7±0.47	69.2±3.7	81.3±5.8	89.3±3.9	94.8±5.7	100.2±6.2	102.8±4.9	104.5±7.5
	setting rate										71.3±6.1%

The aboveground shoot consists of both stem and leaf.

Table S4. The concentration of DP in roots (C_{root}), shoots (C_{shoot}), and leaves (C_{leaf}) and calculated translocation factor (C_{shoot}/C_{root}, (TF_s)) (DW).

soil		Cultivation time (day)									
		15	30	45	60	75	90	105	120	135	150
S1	C_{root}	0.40±0.03	2.13±0.41	4.36±0.38	10.24±1.42	18.32±1.45	23.70±2.12	24.30±2.15	21.61±1.88	22.42±1.88	20.22±1.66
	C_{shoot}	0.02±0.01	0.53±0.05	0.71±0.05	1.22±0.08	1.85±0.13	2.60±0.18	2.63±0.17	2.40±0.12	2.21±0.13	1.92±0.17
	C_{leaf}	-	-	-	-	-	-	-	-	-	-
	TF_s	0.03	0.030	0.045	0.048	0.055	0.056	0.049	0.043	0.039	0.039
S2	C_{root}	2.68±0.03	10.52±1.12	14.77±1.07	25.41±1.98	48.36±3.95	66.32±5.96	71.86±5.58	76.35±4.32	74.12±6.37	70.83±5.68
	C_{shoot}	0.16±0.02	0.70±0.06	1.38±0.12	2.66±0.31	3.48±0.22	3.60±0.27	3.28±0.26	2.74±0.15	2.58±0.18	2.22±0.13
	C_{leaf}	-	-	-	0.03±0.01	0.03±0.01	0.04±0.01	0.05±0.01	0.05±0.01	0.06±0.01	0.06±0.01
	TF_s	0.060	0.067	0.093	0.105	0.072	0.054	0.046	0.036	0.035	0.031
S3	C_{root}	25.43±0.02	45.69±5.52	108.39±9.37	172.92±15.32	205.69±10.51	341.53±23.21	426.93±22.34	469.08±30.62	447.28±21.33	409.92±39.52
	C_{shoot}	0.32±0.03	1.05±0.07	1.95±0.22	3.82±0.29	9.37±1.03	11.92±1.22	12.18±1.18	11.45±1.25	10.82±1.12	10.20±0.89
	C_{leaf}	-	-	-	0.13±0.03	0.17±0.03	0.26±0.04	0.30±0.03	0.33±0.03	0.35±0.02	0.36±0.02
	TF_s	0.012	0.023	0.018	0.022	0.046	0.035	0.029	0.024	0.024	0.025

No DP was detected in roots and shoots from non-spiked control soil.

Table S5. The residual concentrations of DP in each compartment on sampling days in the S1, S2, and S3 soils (DW).

Soil	Layer (mm)	Cultivation time (day)									
		15	30	45	60	75	90	105	120	135	150
S1	Root	95.1±5.8	92.0±6.1	84.3±5.8	75.0±6.9	64.0±3.8	55.2±4.9	50.9±5.2	47.0±3.6	45.3±4.4	43.6±3.8
	1	96.1±6.2	92.8±3.7	86.9±4.2	78.0±5.7	66.7±5.2	59.0±5.5	54.7±4.9	50.9±3.9	47.3±3.9	45.1±3.2
	2	96.2±6.9	93.6±6.3	91.4±6.3	85.8±4.3	80.1±6.6	73.8±6.6	70.0±4.7	66.8±5.7	64.7±5.6	62.6±4.6
	3	97.4±5.1	94.4±5.2	92.3±8.1	88.4±7.5	83.3±3.4	79.0±6.2	76.4±6.8	73.2±5.3	71.3±4.9	69.8±5.7
	4	97.1±7.8	94.2±7.1	90.3±8.7	87.6±9.3	83.0±4.4	80.7±5.9	77.7±7.3	75.2±6.9	73.0±5.4	70.3±5.2
	5	97.2±10.3	94.6±4.4	90.2±5.9	88.1±6.1	84.3±5.6	81.2±7.1	78.4±6.4	76.2±5.4	73.4±4.8	71.8±5.9
	6	97.2±8.3	95.9±8.3	91.4±6.6	90.3±7.3	87.5±7.0	88.3±7.8	85.8±7.6	83.4±5.5	79.3±5.8	77.6±6.8
	7	97.0±4.9	96.1±8.1	95.3±5.1	93.3±7.7	91.7±8.2	91.6±5.8	90.5±5.7	89.2±7.7	86.3±7.4	84.7±7.2
	8	97.0±5.4	96.2±5.6	96.1±10.3	95.7±10.1	94.1±8.8	93.4±6.2	92.1±6.9	90.9±7.6	88.6±4.7	87.7±7.5
	9	97.1±6.2	97.1±6.8	96.0±6.9	96.4±5.9	95.1±6.6	94.1±6.3	92.8±8.3	91.7±8.3	89.5±9.1	89.3±8.6
	10	97.1±6.7	97.1±8.6	96.5±9.6	96.4±5.3	96.1±7.2	95.1±7.9	94.3±8.7	92.9±8.1	90.7±8.5	90.7±8.1
S2	Root	973.3±58.9	952.4±66.3	789.2±52.1	687.5±53.2	605.6±33.3	555.6±54.6	535.1±39.5	524.8±44.4	519.7±39.5	515.1±39.6
	1	975.5±40.2	955.5±73.4	803.1±52.0	698.3±51.9	626.2±43.6	577.6±43.7	563.8±55.2	549.7±54.4	538.8±46.7	529.5±45.5
	2	977.1±32.8	961.5±56.2	874.7±63.2	802.9±61.2	749.2±68.2	702.7±39.8	681.1±53.7	655.8±45.6	643.2±42.5	636.4±49.6
	3	977.8±39.6	964.4±63.7	912.3±48.9	870.7±77.8	825.1±47.9	786.7±46.3	765.3±49.9	747.2±65.2	721.5±63.1	693.3±51.3
	4	978.2±57.9	964.3±49.3	926.7±88.6	898.9±46.9	862.2±51.3	841.3±51.2	812.1±63.2	802.8±63.7	776.6±56.6	752.3±37.8
	5	977.8±63.2	965.3±66.9	936.2±79.2	909.8±57.2	883.3±76.8	868.7±53.6	841.2±69.8	832.4±69.9	822.8±75.3	805.7±42.5
	6	978.3±49.8	964.6±75.6	941.1±66.8	920.8±63.1	897.2±54.3	888.6±69.6	870.8±65.5	862.9±56.8	849.3±71.2	833.2±33.3
	7	977.8±37.1	965.8±56.8	945.3±71.3	928.4±42.6	910.1±49.5	895.7±71.5	893.3±58.9	887.7±69.7	881.2±55.7	869.3±59.6
	8	978.3±90.5	965.8±76.1	947.2±74.5	932.6±56.6	917.3±43.5	905.1±47.8	903.4±75.1	896.8±85.4	892.3±58.9	885.2±58.1
	9	978.1±83.2	966.6±81.2	949.3±81.8	935.4±57.9	920.9±68.8	911.7±59.7	909.2±82.3	903.8±63.8	899.1±62.2	897.4±79.3

	10	978.1±78.7	965.8±59.8	949.2±59.6	935.7±83.7	924.3±82.6	917.3±75.3	912.2±65.7	907.9±73.5	903.6±89.3	901.1±47.9
S3	Root	9856.8±699.6	9736.2±735.6	8970.9±106.9	8758.1±336.9	8614.6±846.3	8241.2±212.3	7864.7±335.2	7842.4±368.9	8702.8±555.2	7536.0±869.2
	1	9871.2±598.3	9761.8±632.5	9142.7±577.5	9364.4±375.1	9256.1±352.4	8745.9±552.5	8699.0±587.5	8601.6±662.5	8548.4±812.3	8432.7±538.7
	2	9878.6±653.1	9811.7±223.8	9422.3±921.7	9390.4±296.8	9254.1±563.6	9045.8±769.3	8911.9±235.8	8754.3±358.4	8715.4±686.9	8597.6±276.3
	3	9882.4±765.9	9835.8±325.8	9576.3±845.5	9481.0±577.3	9314.7±369.7	9296.5±159.4	9256.1±176.9	9153.9±467.8	8843.3±581.4	8745.6±587.7
	4	9884.6±355.2	9845.2±759.6	9636.6±367.2	9562.1±579.6	9532.8±813.2	9464.5±998.7	9287.4±477.5	9235.8±763.2	9204.3±349.6	9012.2±231.8
	5	9888.5±369.4	9851.3±787.5	9686.8±696.8	9599.1±853.2	9575.7±753.8	9503.3±759.2	9442.9±831.3	9325.3±982.3	9210.7±339.2	9176.2±524.6
	6	9888.8±652.4	9854.3±823.1	9728.3±254.3	9616.7±669.7	9531.0±369.4	9472.6±338.2	9388.5±852.1	9301.0±585.1	9201.6±657.6	9156.3±288.6
	7	9890.4±688.2	9856.8±886.9	9757.7±776.9	9633.0±582.2	9595.8±357.9	9552.2±469.6	9474.2±799.6	9352.9±385.7	9334.1±679.1	9256.2±432.5
	8	9892.3±468.7	9858.6±656.7	9774.2±357.8	9654.1±933.2	9622.6±644.3	9588.2±515.8	9518.8±635.9	9294.0±585.1	9366.6±432.5	9274.4±356.7
	9	9892.3±632.9	9861.4±335.2	9781.0±198.8	9664.6±854.1	9642.2±716.9	9578.1±377.5	8524.8±357.2	9486.6±912.7	9388.2±135.6	9311.9±975.3
	10	9892.8±523.4	9861.1±169.7	9791.6±359.6	9665.3±357.9	9651.7±442.8	9575.9±912.1	9537.4±865.7	9498.2±356.9	9401.6±389.5	9332.0±352.3

Table S6. DOC concentrations in each compartment of the rhizobox containing the S1 soil during cultivation (mg/L).

Layer	Cultivation time (day)										
(mm)	0	15	30	45	60	75	90	105	120	135	150
Root	61.0±3.5	60.3±4.7	73.1±3.8	96.3±7.1	110.3±6.6	113.2±8.1	118.6±5.5	125.1±6.5	124.6±7.1	123.0±5.5	119.7±9.6
1	60.4±4.2	60.5±5.1	71.8±6.6	95.0±8.2	108.7±8.9	111.4±7.4	116.1±8.6	123.7±5.4	122.2±5.3	120.3±3.9	116.9±8.1
2	60.0±3.9	60.6± 3.6	69.7±5.5	92.9±6.9	105.8±9.3	109.1±6.4	112.5±9.2	119.7±2.3	117.8±7.4	115.8±6.3	111.0±9.7
3	59.9±5.1	60.6±4.2	67.6±4.2	89.9±4.5	102.0±5.9	103.0±3.5	107.7±6.3	114.3±7.5	108.1±8.6	110.1±2.4	105.0±10.2
4	59.1±5.3	60.6±7.5	63.7±3.9	76.7±4.9	85.3±7.7	86.0±6.1	91.5±7.1	99.4±8.2	98.5±5.8	96.2±1.6	91.4±7.6
5	60.4±4.1	60.6±5.0	61.2±6.2	65.9±3.8	74.5±5.1	75.1±8.1	79.1±5.4	85.6±7.3	84.0±7.5	79.4±5.1	75.1±8.2
6	59.1± 3.6	60.6±6.9	61.2±5.8	63.6±5.7	68.7±6.2	68.0±2.5	72.5±4.9	77.7±8.5	75.9±6.4	70.2±4.3	68.6±7.4
7	59.1±4.9	60.7±7.1	60.3±3.2	61.9±6.2	62.9±3.4	64.2±3.8	67.3±6.8	74.1±2.6	71.3±3.5	67.0±3.6	65.8±6.9
8	60.0± 4.3	60.7±5.7	60.3±4.5	60.2±3.9	60.6±4.7	61.9±5.1	63.2±4.6	70.3±5.5	64.3±2.4	63.3±3.5	63.1±7.5
9	59.2± 4.6	60.7±4.1	59.5±4.6	60.5±5.5	61.1±5.6	61.4±4.2	60.8±3.7	63.9±3.5	63.7±5.4	63.1±2.6	62.6±5.8
10	60.6± 2.8	60.7±5.8	59.5±5.7	60.2±5.8	60.1±5.2	60.4±5.8	62.2±2.9	61.7±6.4	61.1±2.6	60.7±2.9	60.4±6.1

Table S7. K values of fractions transformation of DP on the 150th day.

Parameter	K values with proximity to roots (day $^{-1}$)		
	0 mm (root)	2 mm	10 mm
K_1	0.0295	0.0270	0.0467
K_2	0.0230	0.0106	0.0067
K_3	0.0095	0.0158	0.023
K_4	0.0500	0.0478	0.0134
K_5	0.0050	0.0055	0.0068
K_6	0.0280	0.0241	0.0220

Table S8. Respective contributions of microbial degradation, plant uptake, mobility and bound-residue formation to DP dissipation in soil.

Distances to roots (mm)	Respective contributions to DP removal (%)				
	Excitation effect			Aging effect	Total dissipation
	Mobility ($\times 10^{-2}$)	Microbial degradation	Plant uptake	Bound-residue formation	
0	0.60	54.14	3.85	3.64	61.58
1	0.20	52.90	1.72	4.67	59.46
2	0.20	43.54	0.00	5.85	49.39
3	0.13	36.64	0.00	7.91	44.55
4	0.10	32.21	0.00	10.06	42.27
5	0.04	26.70	0.00	12.00	38.70
6	-0.10	21.37	0.00	13.26	34.63
7	-0.11	16.30	0.00	15.13	31.43
8	-0.19	12.22	0.00	15.88	28.10
9	-0.24	9.49	0.00	16.43	25.92
10	-0.18	8.33	0.00	16.21	24.53

The positive and negative values of mobility represent the efflux and influx of DP in the soil caused by diffusion, respectively.

Table S9. The stereoselectivity of DP in plant tissues and DP fractions in the root compartment, evaluated by the syn-DP isomer fractional abundance (f_{syn}), which was calculated as the concentration of syn-DP divided by the total DP concentrations (DW).

soil			Cultivation time (day)										
			0	15	30	45	60	75	90	105	120	135	150
S1	Tissues	root	-	0.27	0.29	0.34	0.38	0.41	0.43	0.44	0.45	0.46	0.46
		shoot	-	0.25	0.26	0.27	0.3	0.32	0.33	0.34	0.34	0.35	0.35
	DP Fractions	labile	0.25	0.26	0.28	0.32	0.34	0.36	0.38	0.39	0.40	0.40	0.41
		Bound-residue	0.25	0.24	0.23	0.22	0.20	0.18	0.17	0.16	0.16	0.15	0.15
S2	Tissues	root	-	0.26	0.27	0.29	0.32	0.35	0.37	0.39	0.4	0.42	0.43
		shoot	-	0.25	0.25	0.26	0.28	0.31	0.33	0.34	0.35	0.35	0.35
	DP Fractions	labile	0.25	0.26	0.27	0.29	0.33	0.35	0.37	0.38	0.38	0.39	0.39
		Bound-residue	0.25	0.25	0.24	0.23	0.21	0.19	0.18	0.17	0.16	0.16	0.15
S3	Tissues	root	-	0.26	0.27	0.29	0.32	0.34	0.37	0.38	0.39	0.39	0.4
		shoot	-	0.25	0.25	0.27	0.29	0.32	0.34	0.35	0.36	0.36	0.37
	DP Fractions	labile	0.25	0.25	0.26	0.28	0.31	0.32	0.33	0.34	0.34	0.35	0.35
		Bound-residue	0.25	0.25	0.23	0.21	0.19	0.18	0.18	0.17	0.17	0.16	0.16

The f_{syn} value of the commercial standard is 0.25 in our study.

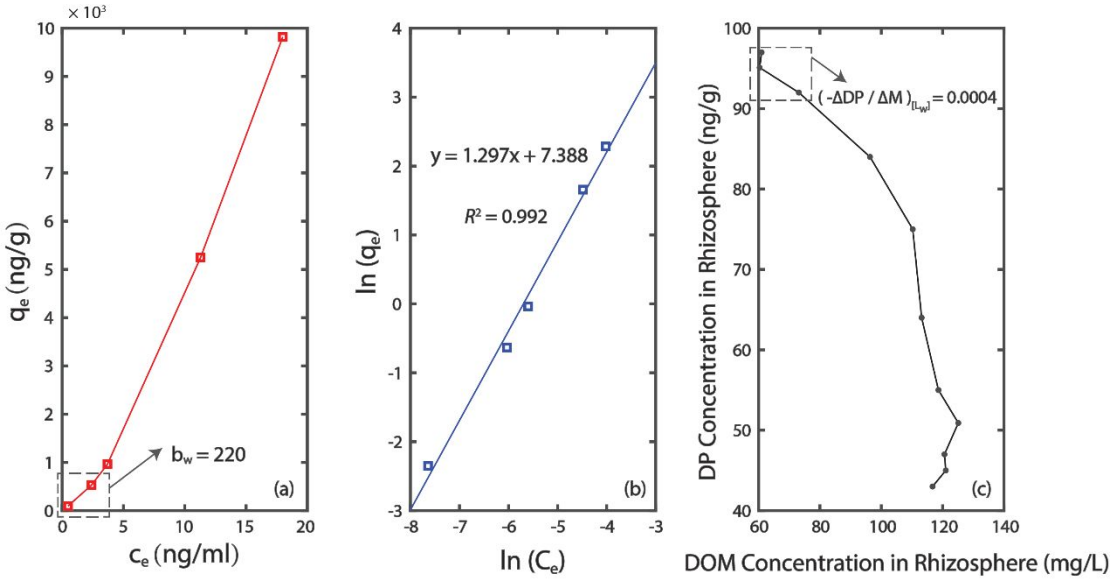

Figure S1. The estimated coefficients in the model, including (a) the sorption curve of DP on soil, (b)the Freundlich adsorption isotherm and (c) the quantity of $(-\Delta DP/\Delta M)_{[L_w]}$.

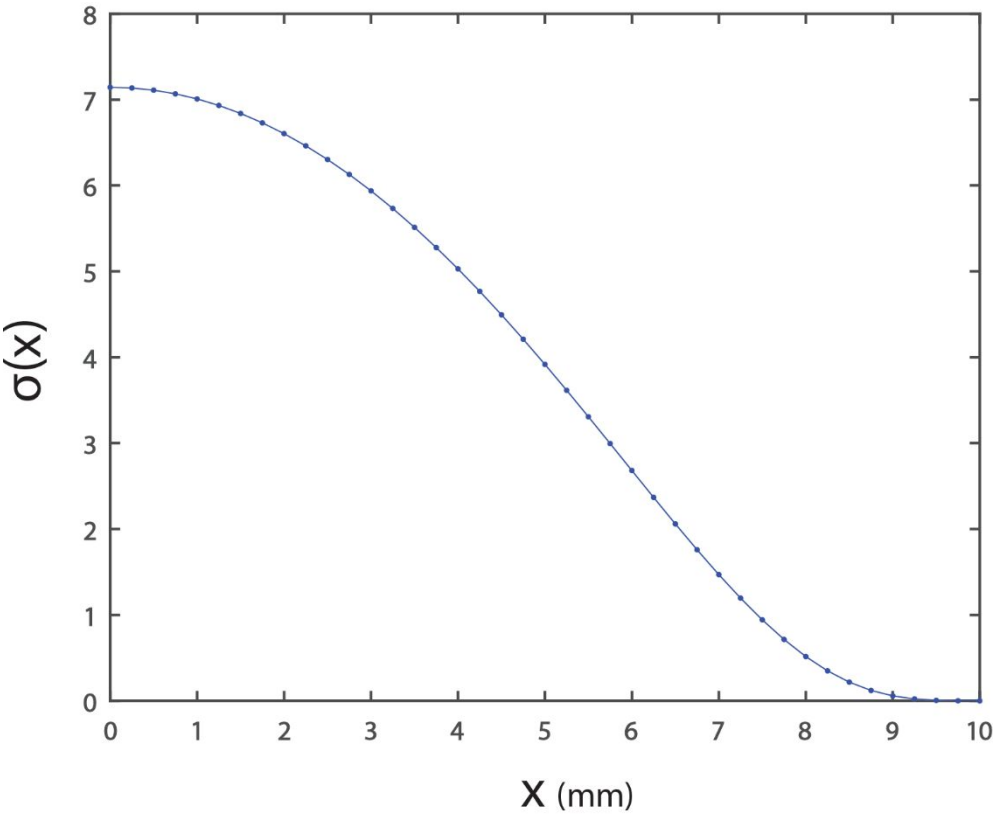

Figure S2. The model simulations for the generation rate of DOC (σ) in soil with distance to roots.

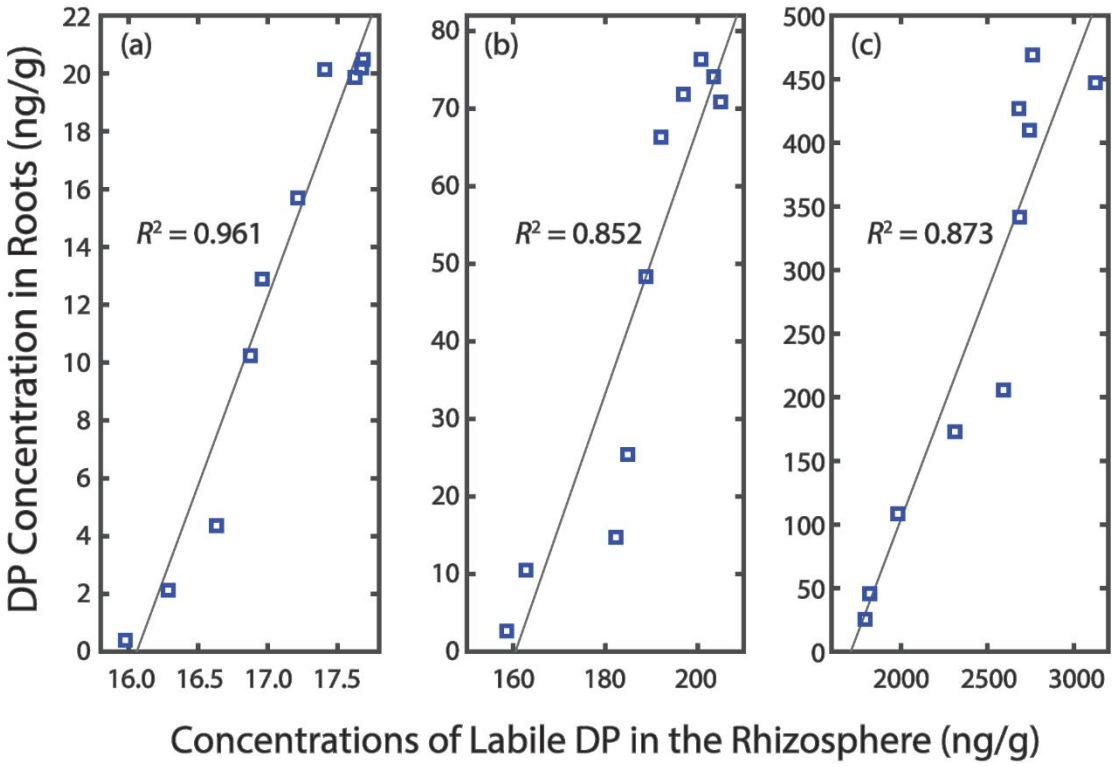

Figure S3. Relationship between the concentration of DP in rice roots and the concentration of labile DP in the root compartment of (a) S1 soil, (b) S2 soil, and (c) S3 soil on dry weight.

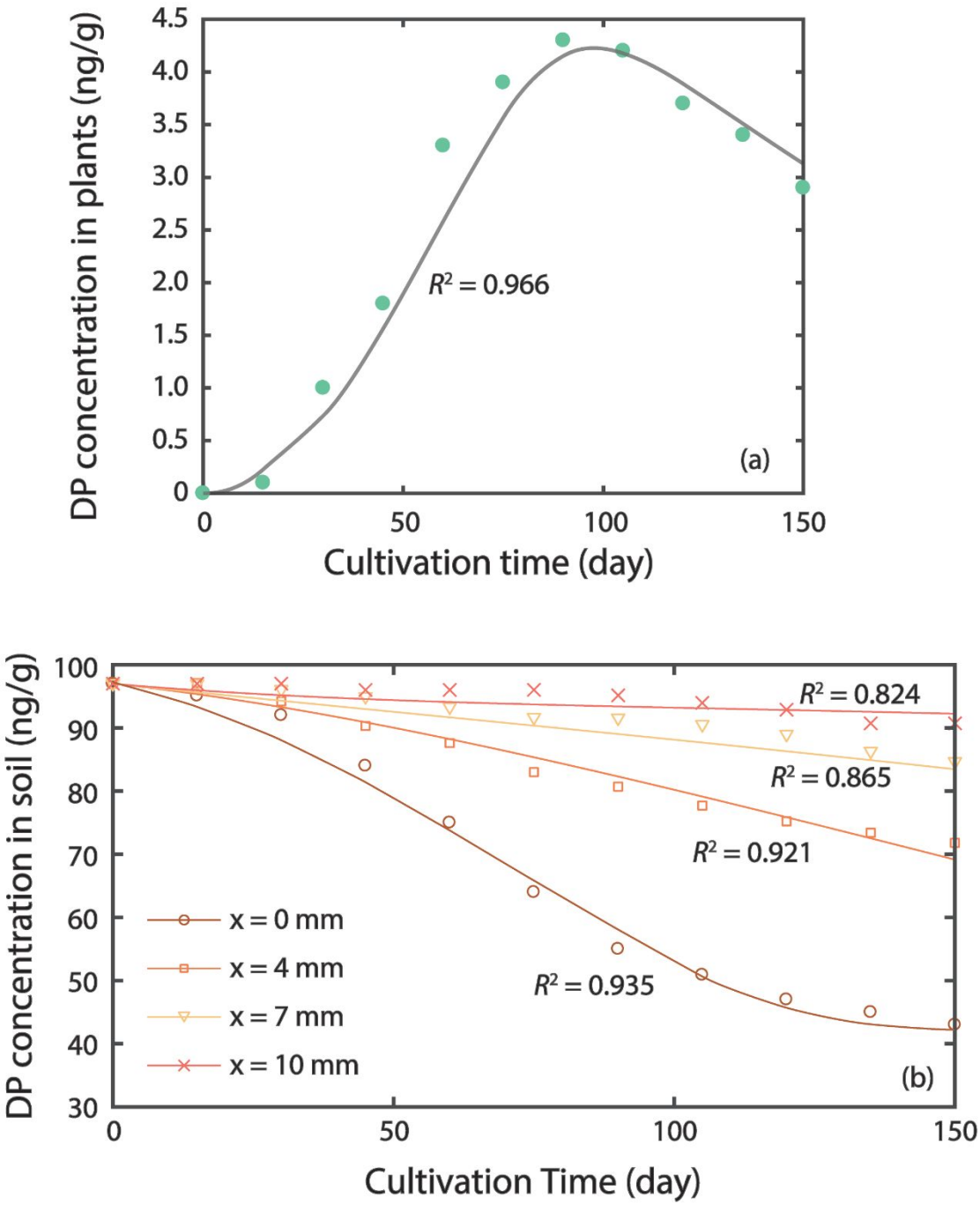

Figure S4. Simulation results of (a) the plant uptake of DP, and (b) residual DP concentrations. Discrete data points represent experimental data, and lines represent model simulations.

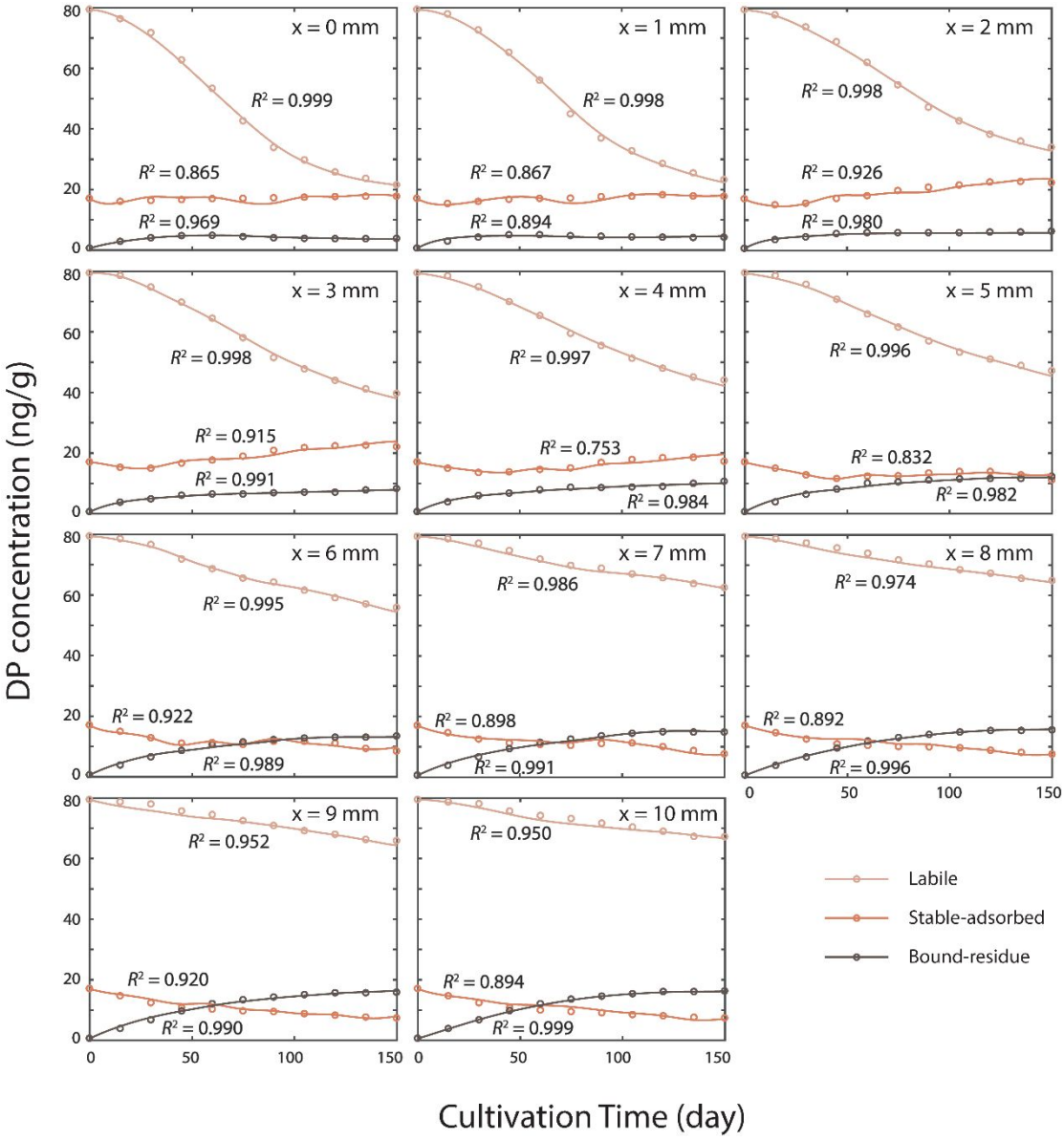

Figure S5. Comparison of simulated and experimental data for the labile, stable-adsorbed, and bound-residue fractions of DP in the rhizosphere during cultivation. Discrete data points represent experimental data, and lines represent model simulations.