Supporting Information

Differential blocking effects of Fe^0 nanoplates on rice accumulation of typical essential and non-essential heavy metal elements in paddy fields

Saiyong Zhu[1,2], Minjie Chen[2], Huiwang Dai[1,2], Saiqa Menhas[1,2], Jiang Xu[2], Daohui Lin[1,2*]

1. Zhejiang Ecological Civilization Academy, Anji 313300, China

2. Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Department of Environmental Science, Zhejiang University, Hangzhou 310058, China

*Corresponding author: lindaohui@zju.edu.cn (Dr. Lin)

Supporting information consists of 18 pages, including 1 text, 5 tables and 14 figures.

Text S1 Rhizosphere injection method of Fe^0 nanoplates

The weight of the topsoil (0-30 cm) was estimated by multiplying the soil density (ca. 2 g cm^{-3}) with the volume, which was about 600 kg m^{-2}. The Fe^0 nanoplate homogenates (12 g L^{-1}) were prepared by diluting the commercial Fe^0 nanoplate slurry with tap water. After then, 18.75 L of the Fe^0 nanoplate homogenates were injected into rice rhizosphere soils in each field plot by a device containing a syringe, a flexible tube, and a steel needle. Specially, the steel needle was designed to have a length of 0.3 m corresponding to the rhizosphere depth of rice plants, and 30 discharge holes distributed spirally on the needle. The injection rate was set as 20 injections per square meter with each injection containing 150 mL of Fe^0 nanoplate homogenates. In this way, plots containing 100 mg kg^{-1} Fe^0 nanoplates in topsoil were obtained. The control (CK) treatment was supplemented with 18.75 L water with the same injection method.

Table S1 Soil physio-chemical properties in the two paddy fields.

	L-R field	H-R field	risk screen threshold	risk control threshold
pH (H_2O)	5.80±0.03	6.02±0.04		
Cd, mg kg^{-1}	2.05±0.35	15.08±1.91	0.4	2.0
Cu, mg kg^{-1}	31.61±2.58	66.65±9.92	50.0	
Zn, mg kg^{-1}	110.20±6.60	254.79±33.66	200.0	
Sand, %	36	39		
Silt, %	32	26		
Clay, %	32	25		

Note: L-R and H-R mean the low-risk and high-risk paddy fields, respectively. Risk screen and control thresholds were set for agricultural soils by the Ministry of Ecology and Environment of China (GB 15618-2018).

Table S2 Recovery rates and the relative standard deviations of target heavy metals from the standard rice and soil samples.

	GBW10045a (rice)			GBW07401a (soil)		
	Certified value, mg/kg	Recovery, %	RSD, %	Certified value, mg/kg	Recovery, %	RSD, %
Cd	0.32±0.04	90-103	4.61	2.5±0.2	92-100	3.08
Cu	2.4±0.2	94-104	4.27	42±5	99-106	3.02
Zn	12.4±1.2	95-106	5.10	475±30	96-101	2.20

Note: GBW10045a (rice) and GBW07401a (soil) are national certified reference materials produced by the Standard Materials Research Center of China.

Table S3 Brown rice yields and thousand kernel weights (TKW) in the two paddy fields after the application of 100 mg kg^{-1} Fe^0 nanoplates at different growth stages.

	Yield, g m^{-2}		TKW, g	
	L-R	H-R	L-R	H-R
CK	1136±39	18.99±0.65	19.83±0.78	1067±42
P0	1367±16**	20.45±0.24**	23.07±0.60*	1242±32**
T1	1559±47**	20.63±0.62**	22.94±1.39*	1247±55**
J2	1229±73*	20.54±1.22	22.50±1.39*	1096±68*
F3	1150±26	19.22±0.44	21.71±1.04	1057±51
GF4	1462±39**	20.61±0.55**	24.16±1.15*	1421±68**

Note: P0, T1, J2, F3, and GF4 mean 100 mg kg^{-1} Fe^0 nanoplate treatments at pre-sowing, tillering, jointing, flowering, and grain-filling stages, respectively. * and ** mean significant differences between different treatments at the confidence levels of 0.05 and 0.01, respectively.

Table S4 Variations of Reproductive mass-Vegetative mass scaling slopes in moderately contaminated (L-R) and highly contaminated (H-R) paddy fields with the application of Fe^0 nanoplates at different growth stages

	L-R			H-R		
	slope	intercept	R^2	slope	intercept	R^2
CK	1.418	-0.023	0.922	1.611	-0.187	0.803
P0	1.139**	0.104	0.892	0.905**	0.059	0.759
T1	1.109*	0.133	0.831	1.121*	-0.051	0.812
J2	1.244	0.114	0.753	1.621	-0.292	0.834
F3	1.155	0.042	0.659	1.491	-0.199	0.781
GF4	1.035**	0.127	0.917	1.186*	0.024	0.869

Note: * and ** mean significant differences between different treatments at the confidence levels of 0.05 and 0.01, respectively.

Table S5 Variations of Grain mass-Vegetative mass scaling slopes in moderately contaminated and highly contaminated paddy fields with the application of Fe^0 nanoplates at different growth stages

	L-R			H-R		
	slope	intercept	R^2	slope	intercept	R^2
CK	1.347	-0.102	0.917	1.717	-0.339	0.784
P0	1.162*	-0.005	0.888	0.923**	-0.055	0.776
T1	1.116*	0.030	0.853	1.167**	-0.175	0.803
J2	1.241	0.012	0.755	1.638	-0.413	0.836
F3	1.229	-0.088	0.644	1.484	-0.324	0.781
GF4	1.011**	0.030	0.915	1.222*	-0.091	0.869

Note: * and ** mean significant differences between different treatments at the confidence levels of 0.05 and 0.01, respectively.

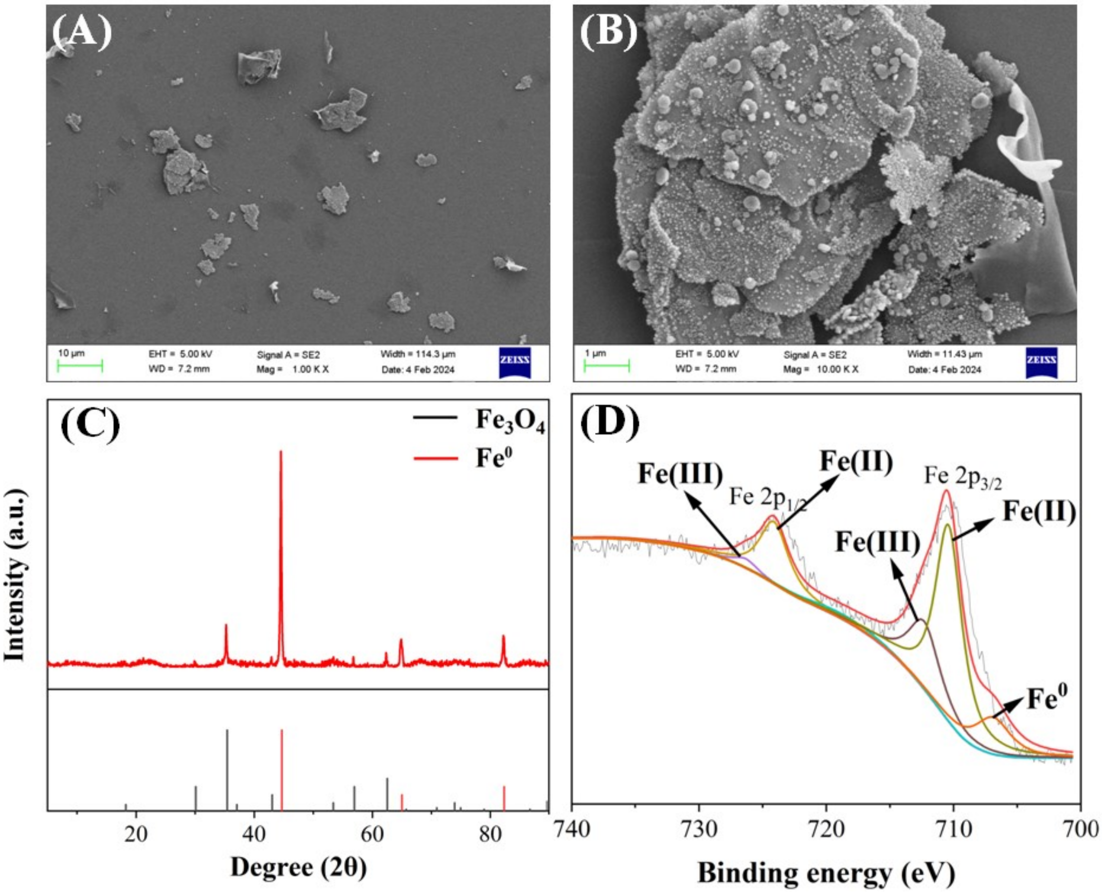

Fig. S1 SEM images (A-B), XRD (C), and XPS (D) analyses of the Fe^0 nanoplates.

Fig. S2 The constructed field plots with rice plants at tillering stage (A), jointing stage (B), and flowering stage (C), and the rhizosphere injection of Fe^0 nanoplates (D).

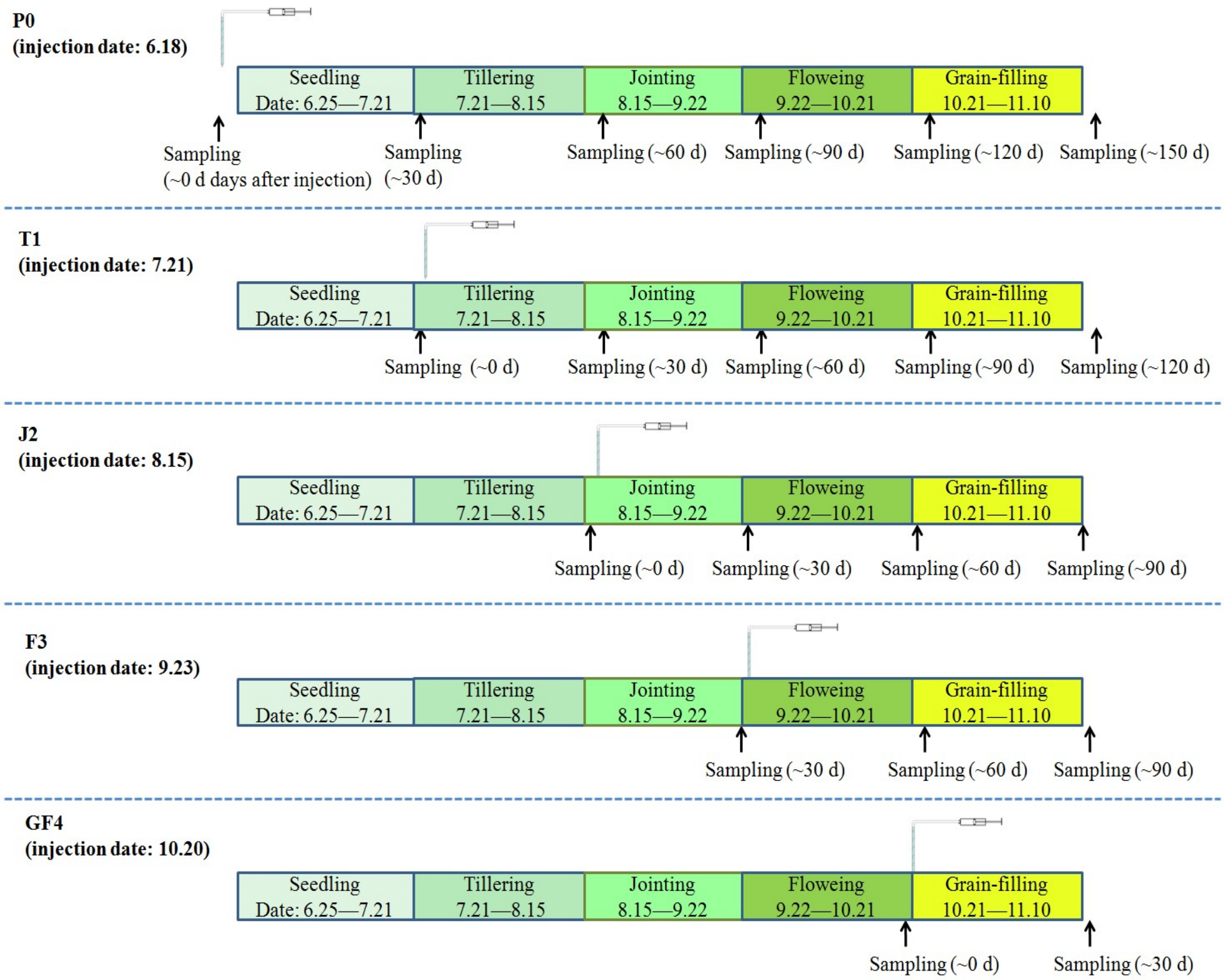

Fig. S3 The schedule of Fe^0 nanoplate treatments and samplings during the rice growth season in the paddy fields in 2023.

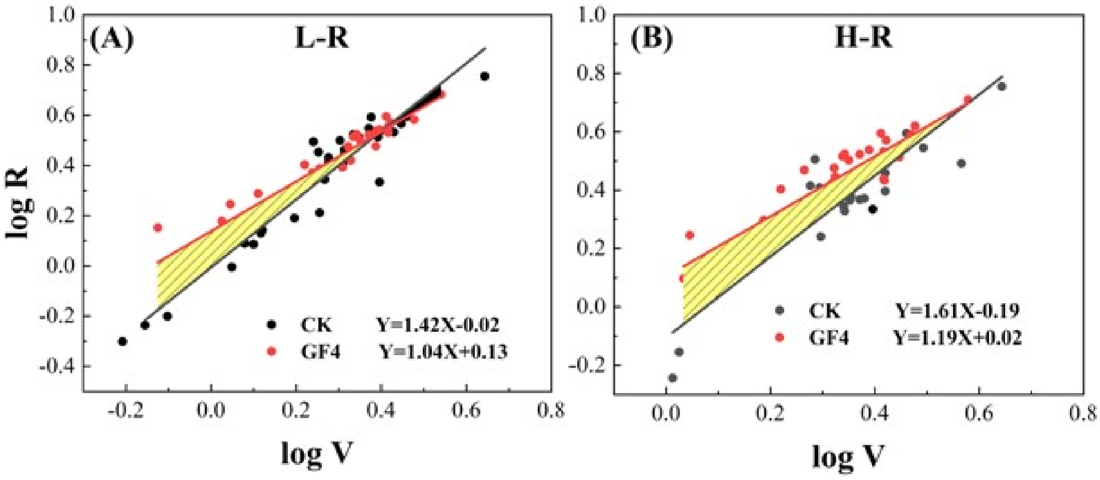

Fig. S4 Bivariate plots of logR-logV scaling relationships of GF4 and CK treatments in L-R field (A) and H-R field (B).

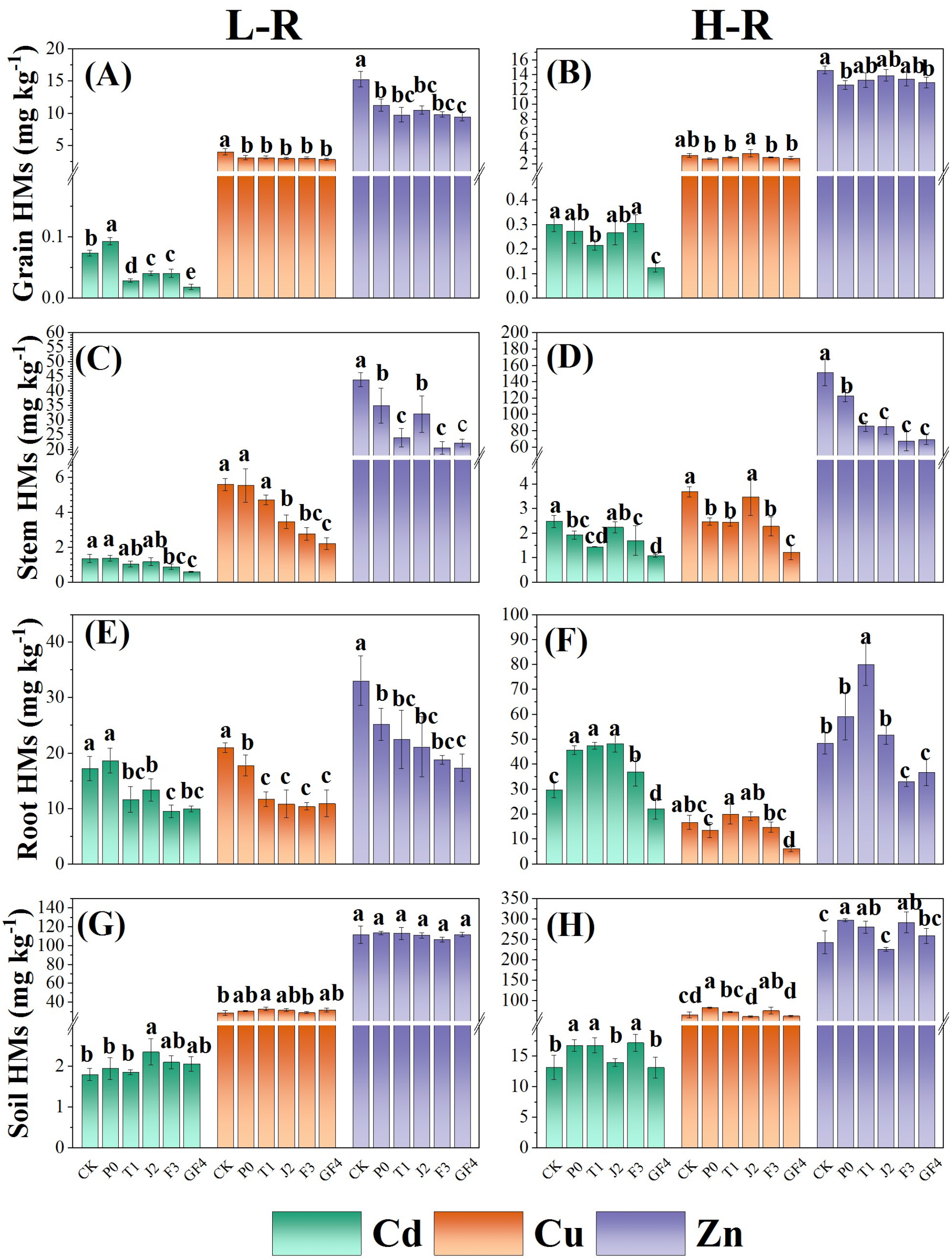

Fig. S5 Variations of Cd, Cu and Zn contents in rice grain (A-B), stem (C-D), root (after DCB extraction, E-F), and soil (G-H) with Fe^0 nanoplate treatment time in L-R and H-R paddy fields. Different letters mean significant differences between the treatments at the confidence levels of 0.05.

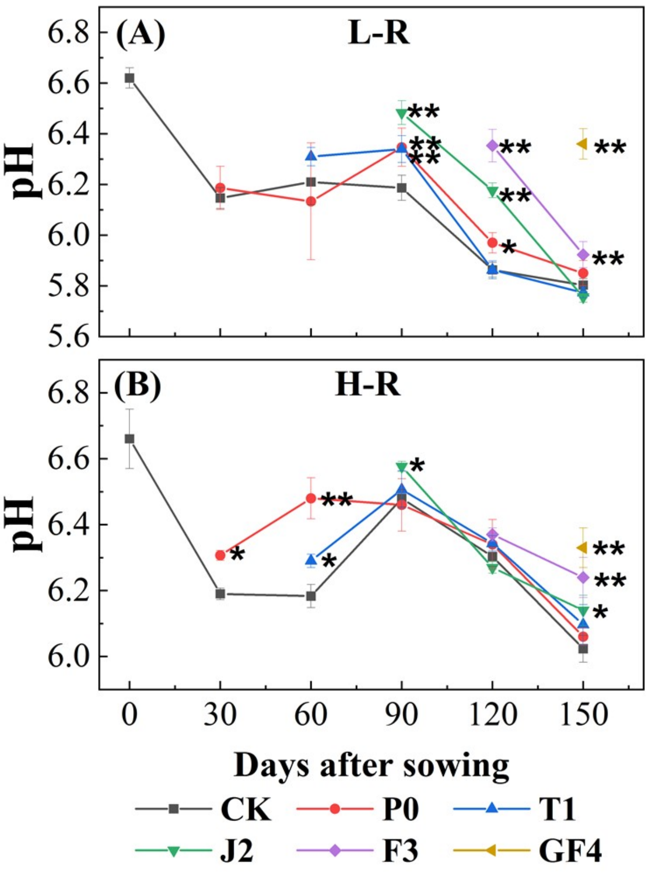

Fig. S6 Changes in rhizosphere soil pH after 100 mg kg^{-1} Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK groups at the confidence levels of 0.05 and 0.01, respectively.

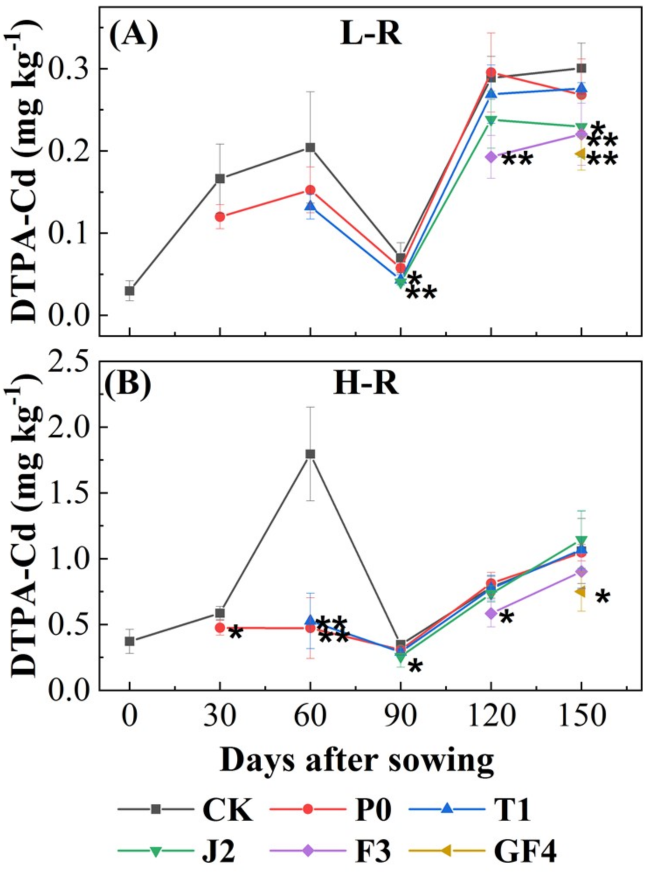

Fig. S7 Changes in rhizosphere soil DTPA-Cd concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK groups at the confidence levels of 0.05 and 0.01, respectively.

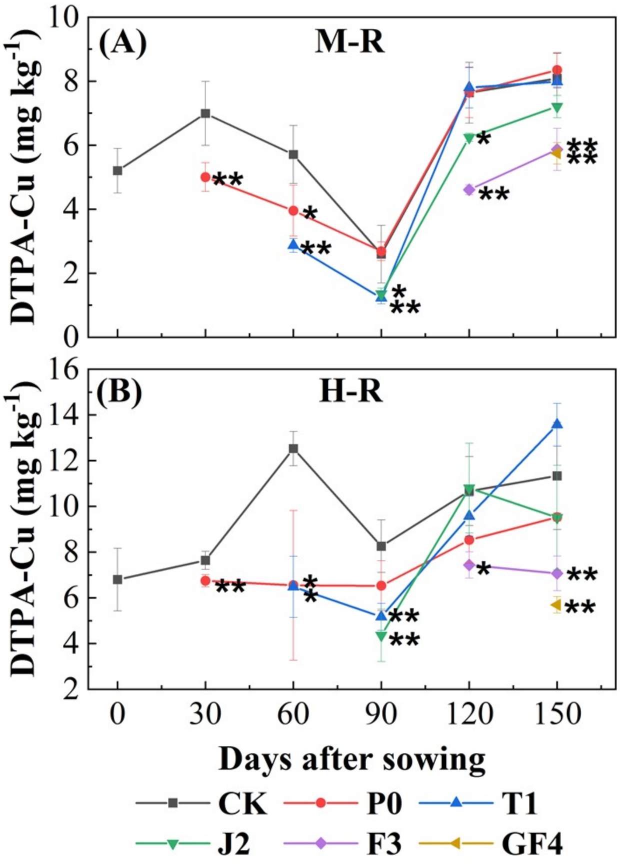

Fig. S8 Changes in rhizosphere soil DTPA-Cu concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK groups at the confidence levels of 0.05 and 0.01, respectively.

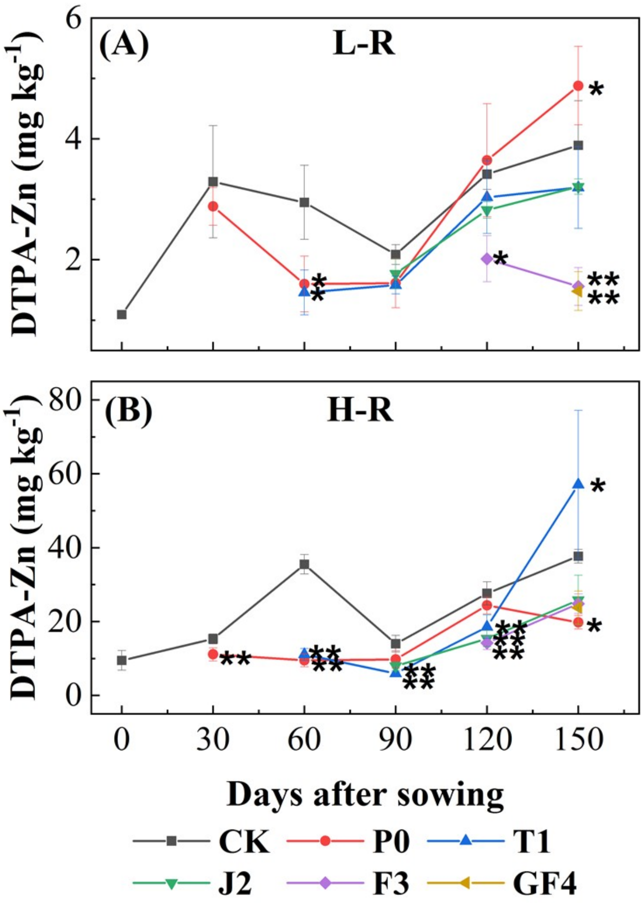

Fig. S9 Changes in rhizosphere soil DTPA-Zn concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK groups at the confidence levels of 0.05 and 0.01, respectively.

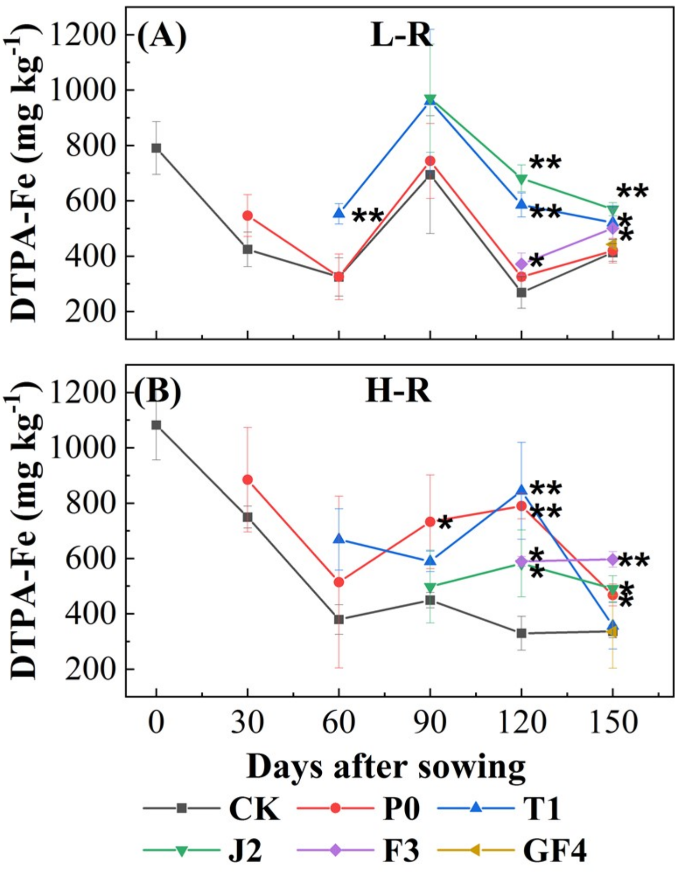

Fig. S10 Changes in rhizosphere soil DTPA-Fe concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK groups at the confidence levels of 0.05 and 0.01, respectively.

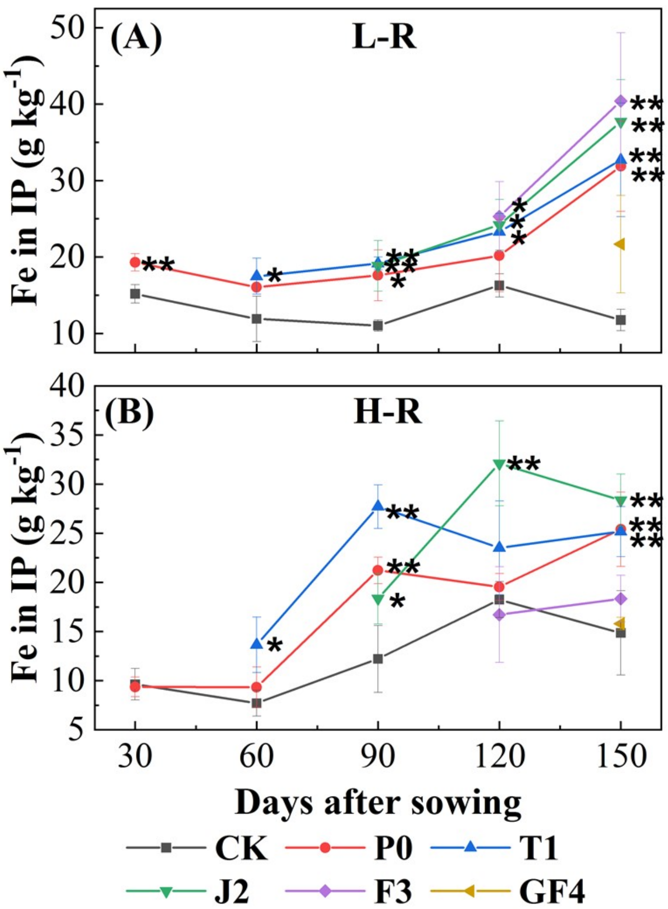

Fig. S11 Changes in IP-Fe concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK treatments at the confidence levels of 0.05 and 0.01, respectively.

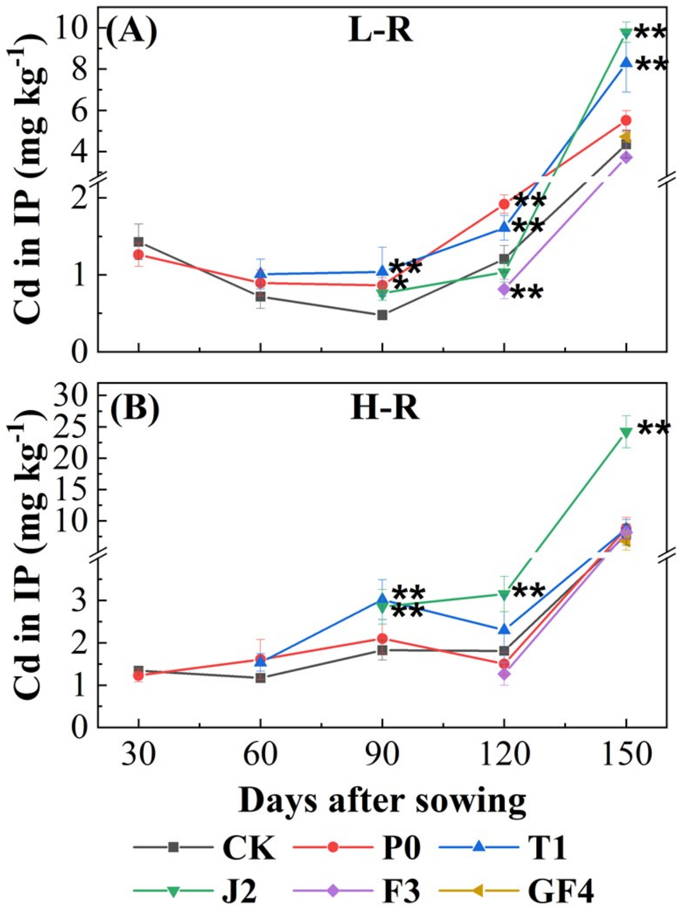

Fig. S12 Changes in root iron plaque (IP)-Cd concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK treatments at the confidence levels of 0.05 and 0.01, respectively.

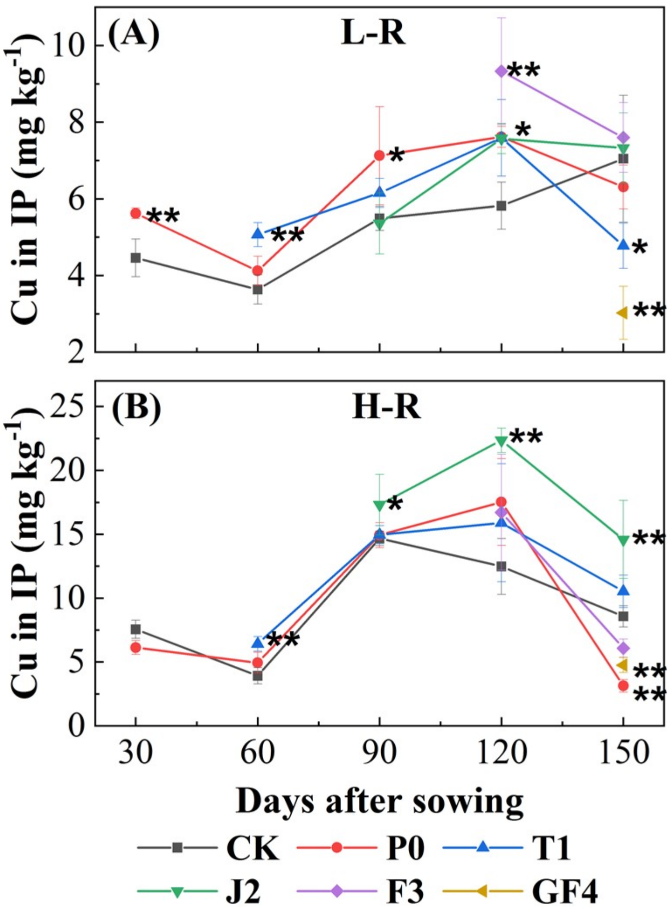

Fig. S13 Changes in IP-Cu concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK treatments at the confidence levels of 0.05 and 0.01, respectively.

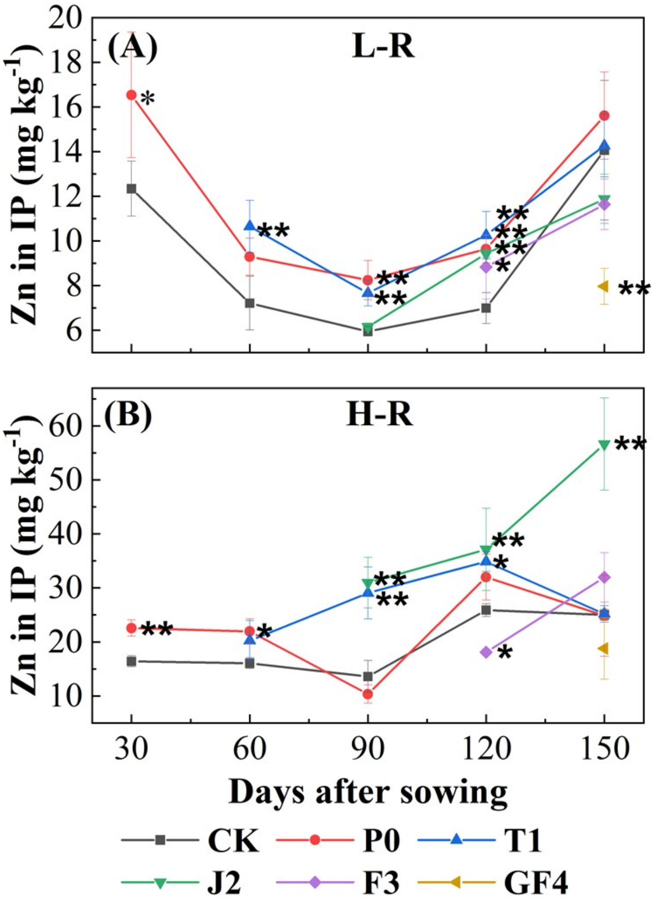

Fig. S14 Changes in IP-Zn concentrations after Fe^0 nanoplate treatments during rice growing in L-R (A) and H-R (B) paddy fields. * and ** mean significant differences between the Fe^0 nanoplate treatments and the corresponding CK treatments at the confidence levels of 0.05 and 0.01, respectively.