Supplementary information

Distribution, bioaccumulation, and trophic transfer of palladium-doped nanoplastics in a constructed freshwater ecosystem

Shuai He,[a] *Hai-Yuan Chi,*[a] Chengjun Li,[a] *Yan Gao,*[b] *Ze-Chen Li,*[a] *Xiao-Xia Zhou,*[ac] and Bing Yan*[ab]

[a] Institute of Environmental Research at Greater Bay Area, Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China.

[b] School of Environmental Science and Engineering, Shandong University, Qingdao 266237, P.R. China.

[c] Guangdong-Hongkong-Macau Joint Laboratory of Collaborative Innovation for Environmental Quality

[*]**Corresponding author**. Tel.: +86-20-37412113; E-mail: xiaoxiazhou89@126.com

This electronic Supplementary Information document contains:

14 pages

7 figures, and

3 tables.

Contents.

TEM characterization of NPs. Transmission electron microscopy (TEM) was conducted with JEM-2100F (JEOL, Japan) operated at 200 kV. Samples were prepared by dripping 5 μL of PS-Pd dispersion onto a carbon-coated TEM grid (Cu, 200 meshes, Zhongxingbairui Technology Co. Ltd., Beijing, China) and dried at room temperature under vacuum. The size distribution was obtained with Nano Measure 1.2 software and Gaussian fitting. At least 120 particles were counted from multi-picture for each case.

SEM characterization of NPs. SEM samples for the synthesized NPs were prepared by loading the dispersions of NPs (~20 μL) onto a silicon wafer. Then, samples were vacuum dried. For the NPs accumulated by plant species, plant tissues were excised, sectioned into small pieces, frozen in liquid nitrogen and freeze-dried. Then, all the above-mentioned samples were coated with platinum nanoparticles for 80 s by a sputter coater (LEICA EM ACE600). The samples were then examined by a field emission scanning electron microscope (QUANTA FEG 250).

DLS measurements of NPs. The hydrodynamic diameters and Zeta potential ofNPs in ultrapure water were determined using a NanoBrook Omni Particle Sizer (Brookhaven Instruments, Holtsville, NYC). The autocorrelation function was acquired with 20 acquisitions for each run.

Stability of PS-Pd NPs. To investigate the stability of the incorporated Pd, the synthesized PS-Pd NPs dispersed in charcoal-filtered tap water, artificial gastric solution, and simulated intestinal fluid were shaken on an end-over-end shaker for 30 and 49 days. Then, the leached Pd was separated from NPs using centrifugal ultrafilter devices (Amicon Ultra-15 30 kD, Millipore, MA). After centrifugation at 6000 rpm for 10 min, the filtrate was collected and mixed with 0.1 mL of HNO_3 (65%) for ICP-MS analysis.

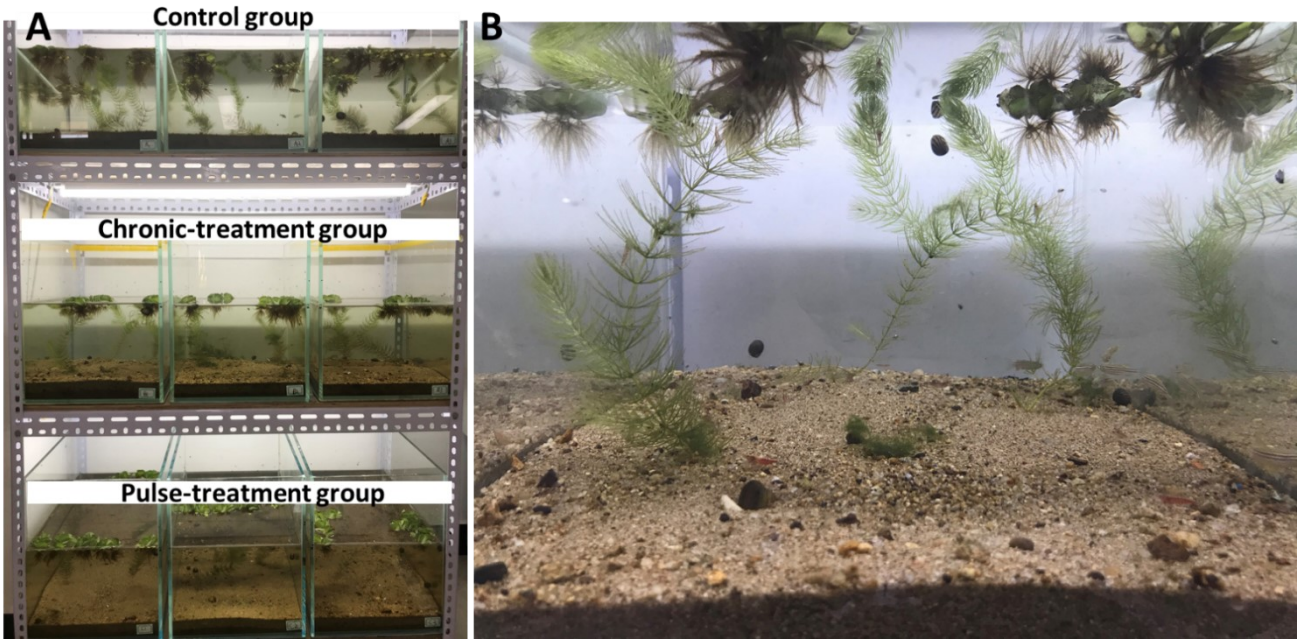

Fig. S1. Optical image of the constructed microcosms during experiment (A) and a typical optical image of the components in a microcosm (B).

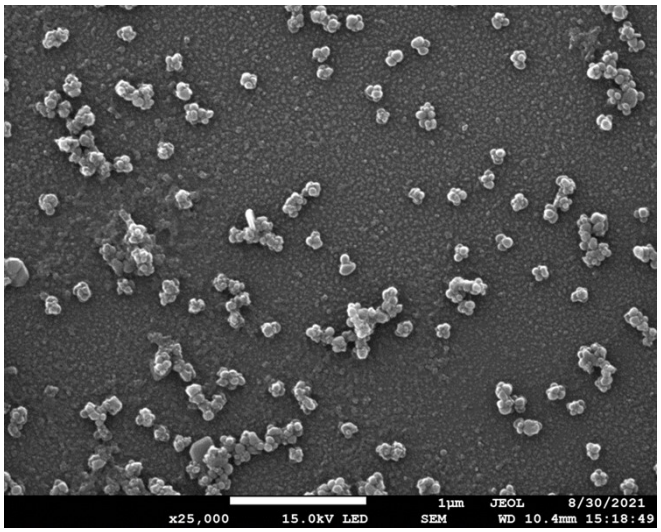

Fig. S2. SEM image of the synthesized Pd-doped NPs.

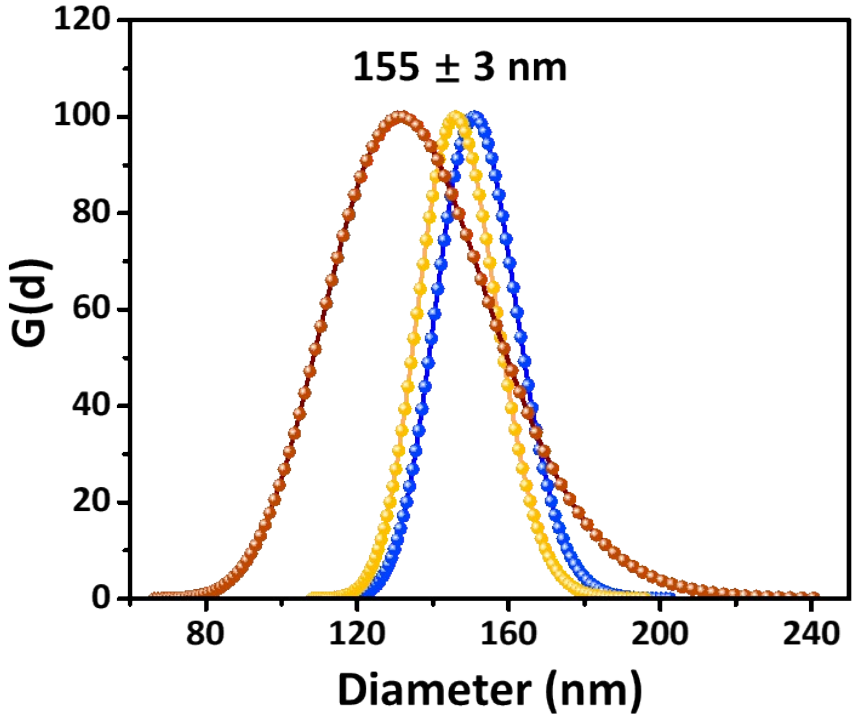

Fig. S3. Hydrodynamic diameters of the synthesized Pd-doped NPs.

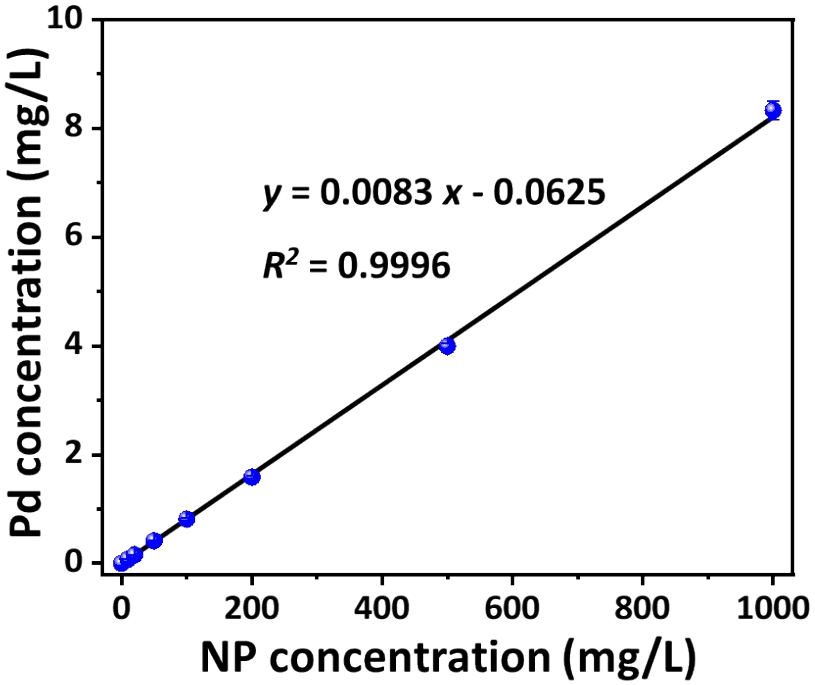

Fig. S4. Measured Pd concentration in Pd-doped NPs with different concentrations.

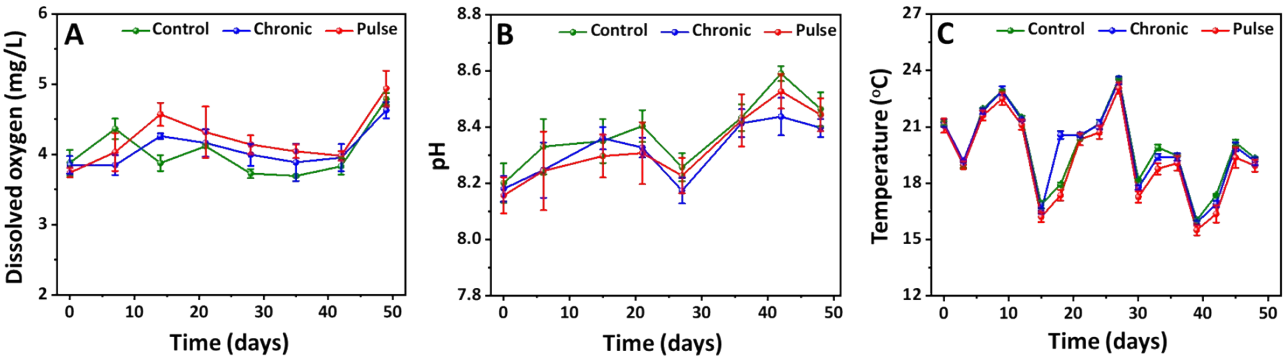

Fig. S5. The dissolved oxygen (A), pH (B), and temperature (C) variations in the constructed microcosms during 49-day exposure (n = 3).

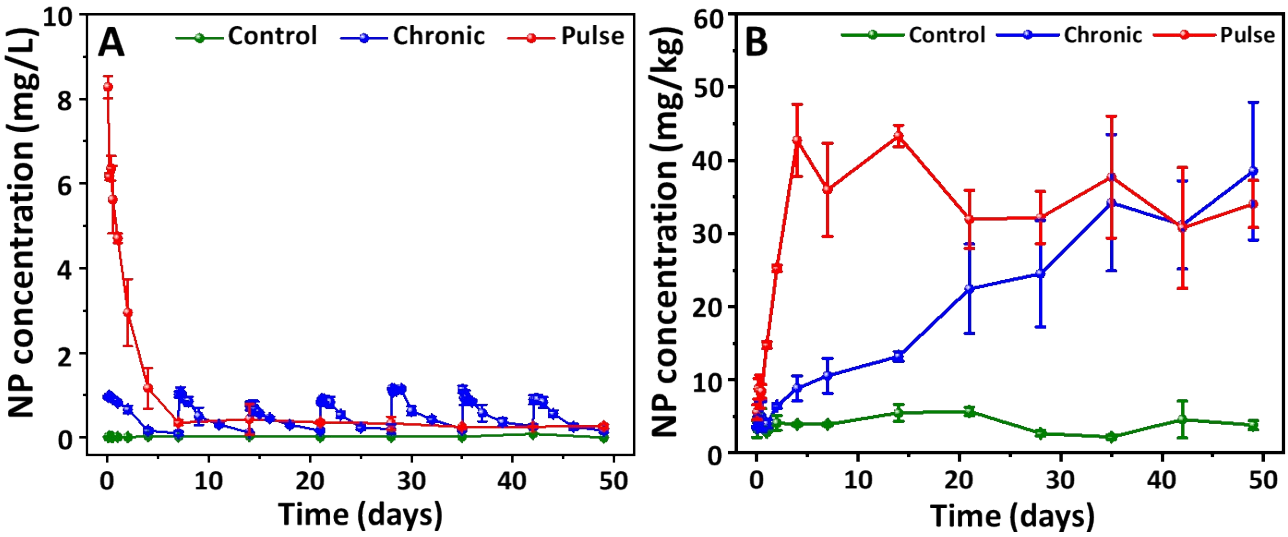

Fig. S6. Time-dependent variations of the Pd-doped NP concentration in water (A) and sediment of the constructed microcosms during 49-day exposure (n = 3).

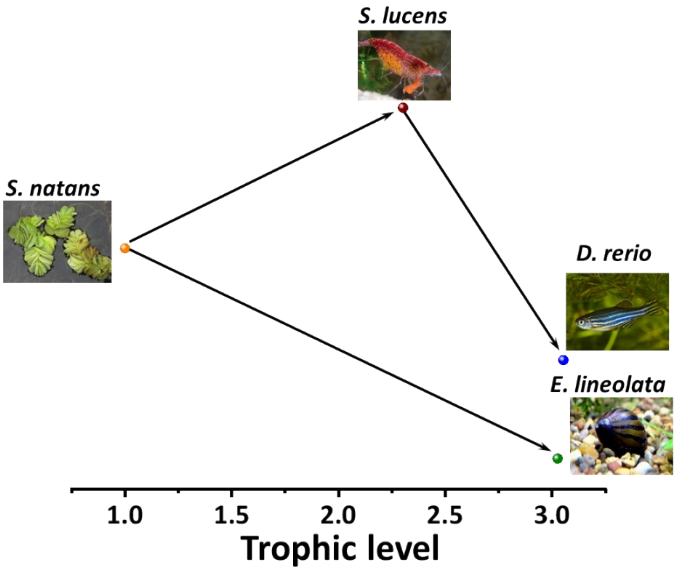

Fig. S7. The trophic relationship among the organisms in the constructed aquatic microcosm.

Table S1. Typical components of a simulated microcosm, and the treatment of organisms after 49-day exposure.

Sample	Mass/Volume/Number	Origin	Age	Treatment after 49-day exposure	
				For NP determination in the whole body	For NP determination in various tissues
Water	23 L	The charcoal-filtered tap water in our lab	-	-	-
Sediments	7 kg	The Pearl River Basin in Guangzhou	-	-	Sediments were collected, freeze-dried and homogenized with a stainless-steel spoon.
D. rerio	7	A market in Guangzhou, China	About 4 months	Two zebrafish in each tank were randomly selected and euthanized instantly. The fish were rinsed with ultrapure water thoroughly, weighed, cut into small pieces with a blade, and then freeze-dried. Finally, the dried samples were weighed and ground into fine powders in a mortar.	Five zebrafish were randomly selected in each tank and euthanized instantly. The fish were rinsed with ultrapure water thoroughly, weighed. and then dissected under a dissecting microscope. Five tissues, including the intestine, liver, brain, gill and muscle were separated, weighed, and the muscle tissue was chopped with a blade. Then, all the tissues were freeze-dried and weighed.
E. lineolatan	3	A market in Guangzhou, China	About 3 months	All the snails were washed several times with ultrapure water, shelled, weighed and then cut into small pieces. Then, the samples were freeze-dried, weighed and ground into fine powders in a mortar.	-
C. fluminea	8	The Dagu River Basin	About 3 months	All the Asian clams were washed several times with ultrapure water, shelled, weighed and then	-

		in Qingdao, China		cut into small pieces. Then, the samples were freeze-dried, weighed and ground into fine powders in a mortar.	
S. lucens	15	A market in Guangzhou, China	About 1 month	Five shrimps were selected randomly, washed thoroughly with ultrapure water, and weighed and cut into small pieces. Then, the samples were freeze-dried, weighed and ground into fine powders in a mortar.	Ten shrimps were selected randomly and thoroughly rinsed with ultrapure water. Then, the shrimps were separated into head and body and weighed. Then, each tissue was freeze-dried, weighed, and ground into fine powders in a mortar.
C. demersum	3	A market in Zhongshan, China	About 40 days	One *C. demersum* was selected randomly, washed with ultrapure water and weighed. Then, the plant was cut into small pieces with a blade, freeze-dried, weighed, and ground into fine powders in a mortar.	Two *C. demersum* were rinsed with ultrapure water, and then divided into upper (about 5 cm below the water surface) and lower tissues. Each tissue was weighed and cut into small pieces with a blade. Then, the sample was freeze-dried, weighed, and ground into fine powders in a mortar.
S. natans	3	Zhongshan	About 40 days	One whole *S. natans* was selected randomly, washed with ultrapure water, and weighed. Then, the sample was cut into small pieces with a blade, freeze-dried, and weighed. Then, the sample was ground into fine powders in a mortar.	Two strains of *S. natans* were rinsed with ultrapure water, divided into leaves and roots, and weighed. Samples were cut into small pieces with a blade, freeze-dried, and weighed. Then, the sample was ground into fine powders in a mortar.

Table S2. Analytical performance of quantification of Pd-doped NPs in different sample matrix with ICP-MS.

Matrix		Range	N	Linearity	R^2	Recoveries (%, n = 3)	*RSD* (%)	*LOD*	*LOQ*
Water		0.2-50 mg/L	8	$y = 1.011\ x - 0.188$	0.9998	76.5–101	0.5–4.0	0.036 mg/L	0.12 mg/L
Sediments		2-100 mg/kg	6	$y = 0.850\ x - 0.17$	0.9999	73.6–85.5	2.0–8.5	0.45 mg/kg	1.49 mg/kg
Biota	Animals[b]	5-500 mg/kg	8	$y = 0.970\ x - 5.169$	0.9996	78.7–98.7	1.2–3.6	0.76 mg/kg	2.53 mg/kg
	Plants[a]	2-500 mg/kg	8	$y = 1.071\ x - 2.088$	0.9940	78.3–110	0.4–7.2	0.44 mg/kg	1.47 mg/kg

[a]using *D. rerio* as aquatic animal species models.

[b]using *S. natans* as aquatic plant species models.

Table S3. Pd leaching from the Pd-doped NPs under different conditions.

Conditions	NP Concentration	Free Pd/total Pd (%)		
	(mg/L)	0-day	30-day	49-day
charcoal-filtered tap water under light	8.4	0.46 ± 0.03	0.48 ± 0.04	0.49 ± 0.03
	1.2	0.43 ± 0.06	0.42 ± 0.03	0.39 ± 0.03
Artificial gastric solution under dark	8.4	0.08 ± 0.01	1.04 ± 0.13	1.19 ± 0.12
	1.2	0.56 ± 0.25	2.46 ± 0.43	3.51 ± 0.32
Simulated intestinal fluid under dark	8.4	0.04 ± 0.01	0.47 ± 0.05	0.47 ± 0.07
	1.2	0.34 ± 0.11	1.31 ± 0.24	1.44 ± 0.25