

Supporting Information

Enhanced toxicity of environmentally transformed ZnO nanoparticles relative to Zn ions in the epibenthic amphipod *Hyalella azteca*

Authors:

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Table S1. Measured total and dissolved Zn concentrations from ZnSO₄ and ZnO NP exposures. In freshwater and saltwater treatments, measured values are shown with standard deviation (??)

A. Freshwater

Treatment (nominal, mg L ⁻¹)	ZnSO ₄		<i>pristine</i> ZnO NP		p6-ZnO NP		p8-ZnO NP		s-ZnO NP	
	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn
0.03	0.03±0.01	0.030±0.003	0.023±0.003	0.02±0.01	0.025±0.005	0.022±0.001	0.03±0.01	0.030±0.005	0.02±0.01	0.008±0.004
0.10	0.10±0.01	0.10±0.01	0.07±0.01	0.07±0.01	0.09±0.01	0.074±0.002	0.09±0.01	0.08±0.02	0.11±0.01	0.02±0.01
0.30	0.28±0.03	0.28±0.03	0.24±0.03	0.21±0.02	0.29±0.04	0.21±0.01	0.33±0.07	0.27±0.03	0.26±0.03	0.04±0.02
1.00	1.02±0.06	1.01±0.08	0.83±0.04	0.40±0.10	1.12±0.20	0.37±0.02	0.99±0.14	0.393±0.003	0.86±0.28	0.07±0.02
3.00	3.12±0.02	1.46±0.51	ND	ND	3.13±0.15	0.53±0.01	3.61±0.43	0.50±0.20	3.22±0.02	0.198±0.004

B. Saltwater

Treatment (nominal, mg L ⁻¹)	ZnSO ₄		<i>pristine</i> ZnO NP		p6-ZnO NP		p8-ZnO NP		s-ZnO NP	
	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn
0.03	0.03±0.03	0.03±0.01	0.03±0.01	0.03±0.01	0.02±0.01	0.020±0.001	0.021±0.005	0.019±0.003	0.028±0.001	0.007±0.001
0.10	0.091±0.003	0.092±0.004	0.07±0.01	0.07±0.01	0.08±0.01	0.066±0.004	0.09±0.01	0.081±0.004	0.11±0.01	0.02±0.01
0.30	0.28±0.01	0.27±0.01	0.25±0.02	0.23±0.01	0.25±0.04	0.20±0.03	0.23±0.05	0.19±0.01	0.31±0.02	0.06±0.05
1.00	0.98±0.01	0.92±0.13	0.82±0.09	0.62±0.10	0.77±0.15	0.48±0.09	0.88±0.27	0.58±0.08	0.97±0.37	0.19±0.10
3.00	3.04±0.24	1.43±0.18	ND	ND	2.92	0.73±0.12	2.58	0.73±0.10	2.79±0.64	0.37±0.25

C. Sediment

Treatment (nominal, mg L ⁻¹)	ZnSO ₄		<i>pristine</i> ZnO NP		p6-ZnO NP		p8-ZnO NP		s-ZnO NP	
	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn
0.1	0.010	0.01	0.006	0.01	0.010	0.004	0.010	0.004	0.013	0.003
0.3	0.019	0.01	0.026	0.02	0.019	0.01	0.019	0.01	0.028	0.004
1.00	0.072	0.05	0.084	0.06	0.069	0.04	0.069	0.04	0.073	0.01
3.00	0.36	0.31	0.40	0.34	0.33	0.21	0.33	0.21	0.38	0.05
10.00	1.64	1.55	1.74	1.46	1.43	1.14	1.43	1.14	0.66	0.19

D. Sediment with Basket

Treatment (nominal, mg L ⁻¹)	ZnSO ₄		<i>pristine</i> ZnO NP		p6-ZnO NP		p8-ZnO NP		s-ZnO NP	
	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn	Total Zn	Dissolved Zn
0.1	0.012	0.01	0.013	0.01	0.010	0.003	0.010	0.003	0.008	0.002
0.3	0.025	0.02	0.026	0.02	0.027	0.02	0.019	0.02	0.019	0.005
1.00	0.11	0.06	0.10	0.09	0.079	0.05	0.069	0.05	0.067	0.01
3.00	0.44	0.41	0.49	0.44	0.35	0.25	0.33	0.25	0.28	0.07
10.00	2.29	1.87	1.68	1.64	1.68	1.46	1.43	1.46	0.88	0.54

Table S2. Concentrations of Zn measured in sediments following sediment exposure**A. Sediment**

Treatment (nominal, mg L ⁻¹)	Mass balance expected Zn (mg kg ⁻¹)*	ZnSO ₄	<i>pristine</i> ZnO NP	p6-ZnO NP	p8-ZnO NP	s-ZnO NP
		Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)
0.0	32.0	34.8±2.2	33.1±2.7	31.1±3.4	30.9±1.1	31.5±0.9
0.1	32.7	35.9±1.2	33.8±2.8	31.9±1.3	32.4±1.2	31.8±1.0
0.3	34.2	37.0±1.6	35.7±1.5	32.9±1.3	36.6±2.2	31.9±3.2
1.00	39.2	41.8±0.9	39.4±0.9	40.2±1.2	40.9±1.8	35.0±1.4
3.00	53.5	60.5±0.6	56.8±1.5	57.7±2.9	55.8±2.4	46.0±5.7
10.00	103.6	110.0±9.8	111.4±5.8	107.4±16.6	106.5±6.4	83.5±15.0

B. Sediment with Basket

Treatment (nominal, mg L ⁻¹)	Mass balance expected Zn (mg kg ⁻¹)*	ZnSO ₄	<i>pristine</i> ZnO NP	p6-ZnO NP	p8-ZnO NP	s-ZnO NP
		Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)	Total Zn (mg kg ⁻¹)
0.0	32.0	32.7±0.8	31.0±0.8	32.4±0.4	30.6±0.9	31.2±1.2
0.1	32.7	35.3±1.6	32.7±1.0	33.8±2.1	31.0±1.5	32.3±1.0
0.3	34.2	39.2±3.7	33.6±0.7	36.7±0.7	32.6±0.7	32.3±0.8
1.00	39.2	44.7±2.4	39.5±1.8	44.1±2.0	39.4±1.6	35.7±2.5
3.00	53.5	62.3±4.7	54.6±1.4	62.5±6.6	58.2±4.3	46.4±2.2
10.00	103.6	108.4±4.8	95.2±2.4	112.9±10.6	105.0±6.3	87.6±12.2

*Mass balance expected Zn was determined by multiplying the concentration by 90% to account for Zn remaining in the water column, then multiplying by 0.175 L to get total Zn added to sediment. Total Zn was divided by 0.022 kg of total sediment added to get an expected sediment concentration. Then 32.0 mg/Kg was added to each concentration to account for background Zn in the sediment.

Figure S1. Powder X-ray fractograms of as-synthesized and transformed ZnO NPs. Note that the p8-ZnO NP fractogram (bottom) only contains peaks for ZnO. This corresponds to the core structure, the $\text{Zn}_3(\text{PO}_4)_2$ shell is amorphous and does not produce a diffraction pattern; however, its presence is confirmed using X-ray absorption near-edge (XANES) spectroscopy and ^{31}P magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) (Rathnayake et al., 2014).

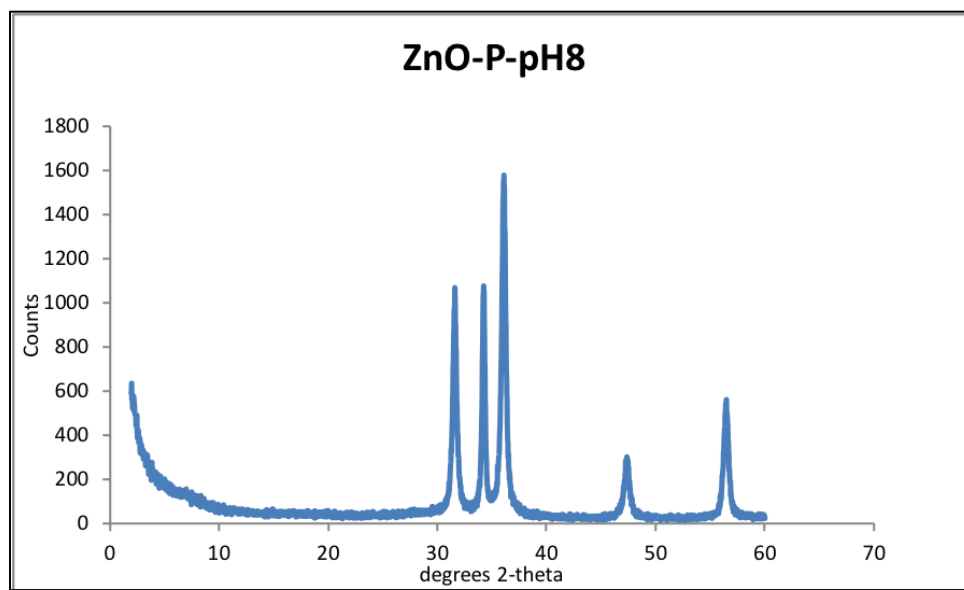
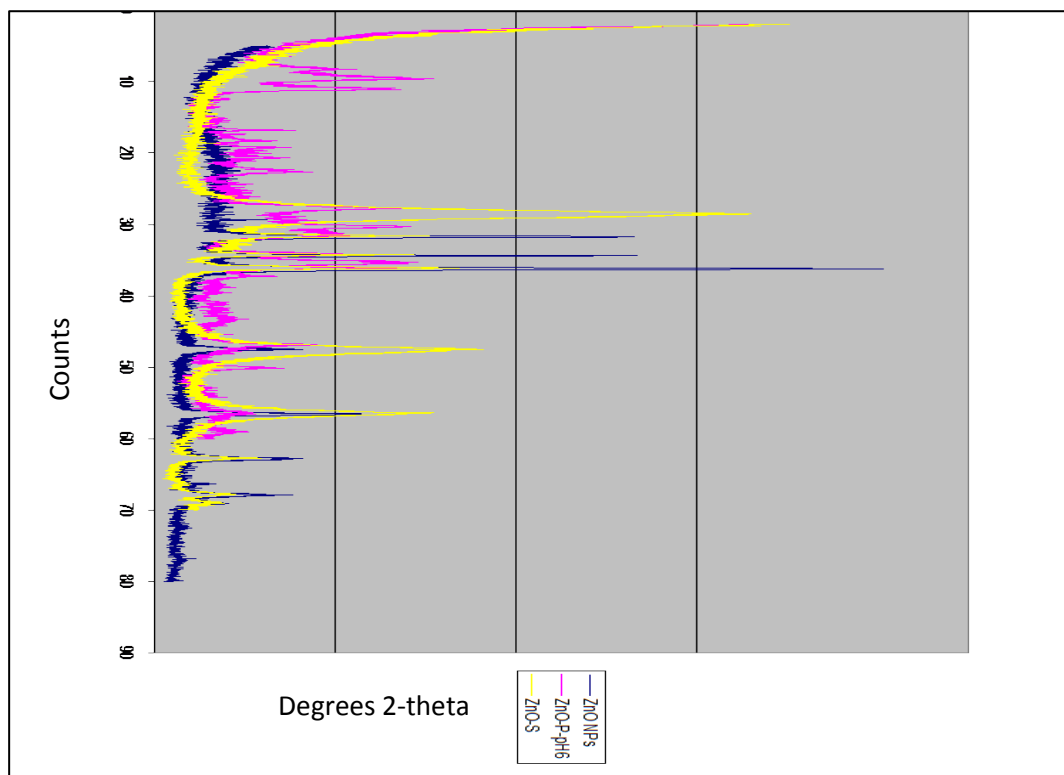
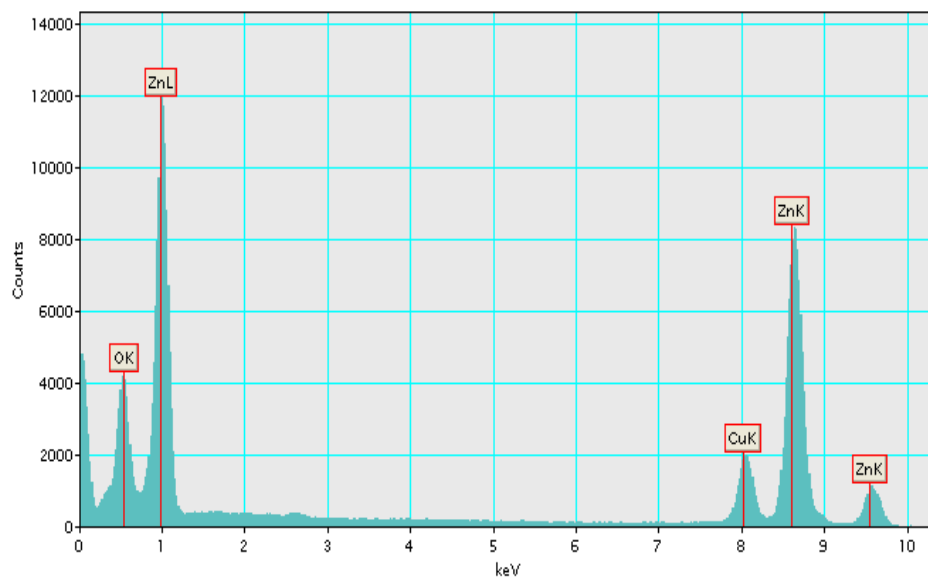
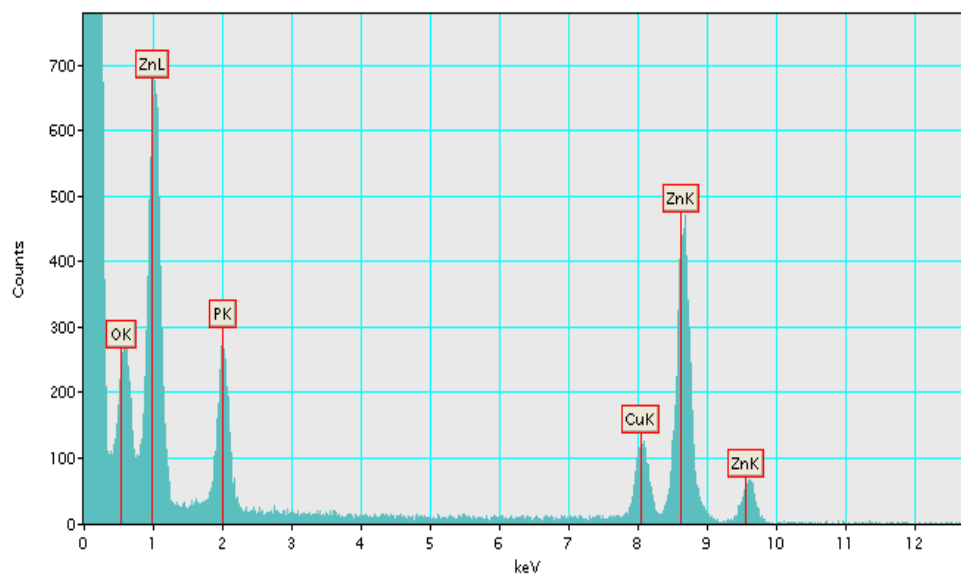


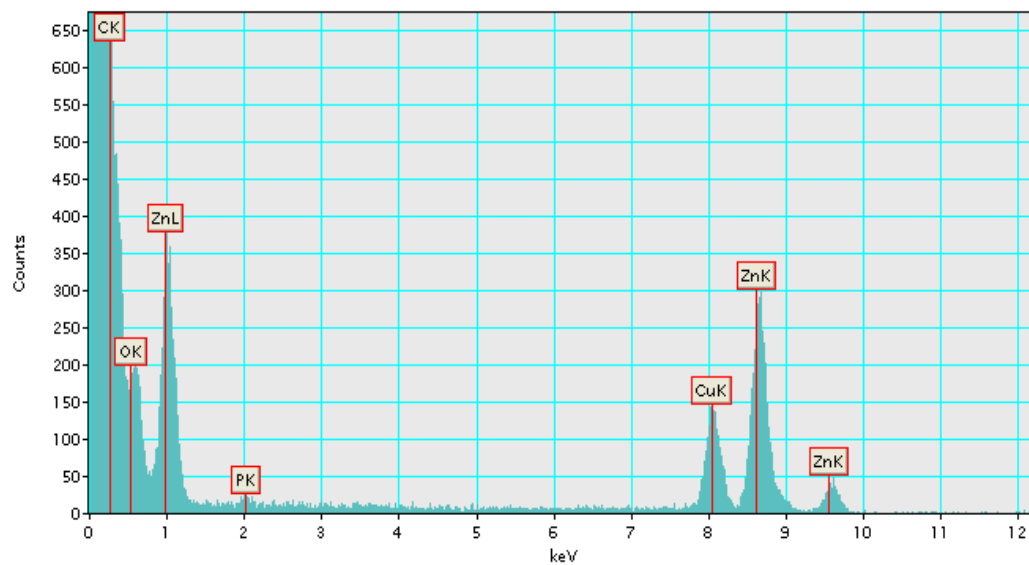
Figure S2. Energy dispersive X-ray spectra of as-synthesized and aged ZnO NPs collected using the transmission electron microscope with probe focused on particles.



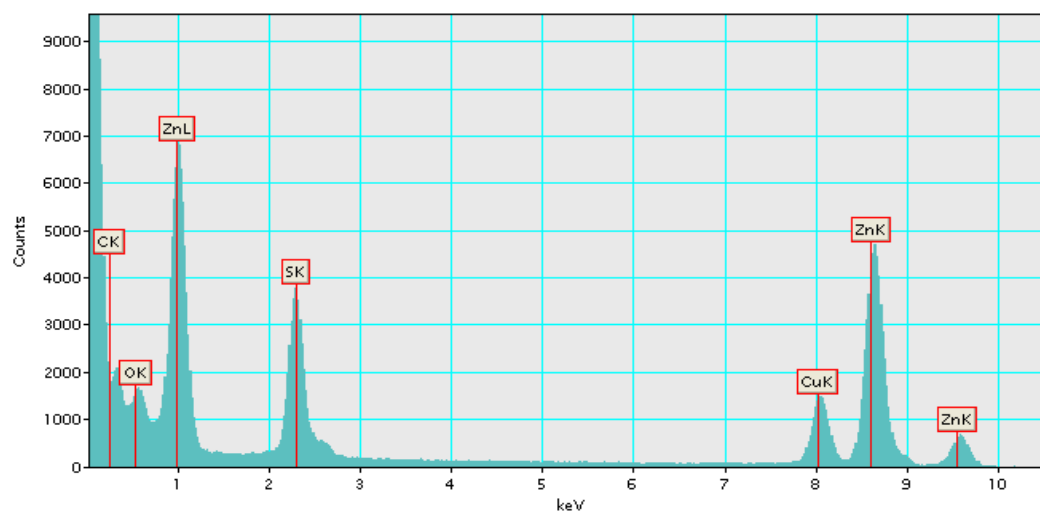
a) ZnO NPs



b) p6-ZnO NPs



c) p8-ZnO NPs



d) s-ZnO NPs