Toxicity of Oxidatively Degraded Quantum Dots

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Contributions of QD or assay components other than Cd and Se to toxicity of weathered QDs. Zebrafish embryos/larvae were exposed to assay components (MHQ-Fe-H_2O_2), $ZnCl_2$ or PEG-thiol at concentrations relevant to those in QD dosing solutions to determine the extent that these components may have contributed to the toxicity produced by weathered QDs. We also examined the toxicity of ethylene glycol (EG) because it is an oxidative breakdown product of PEG.

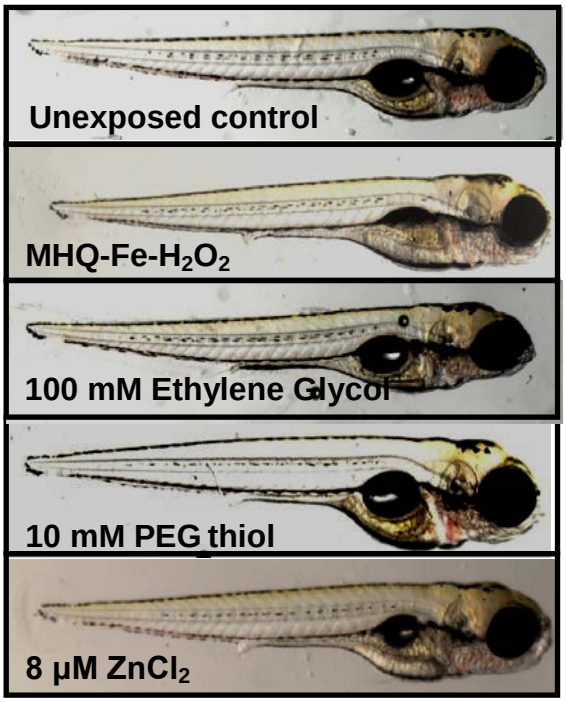

Figure S1. Representative micrographs of zebrafish larvae exposed to concentrations of assay components (MHQ-Fe-H_2O_2), ethylene glycol, oxidized PEG-thiol and $ZnCl_2$ relevant to QD exposures.

Toxicity of (nano)particulate vs. dissolved fraction of weathered QDs. Following MHQ-driven Fenton's reaction exposure, QD solutions were filtered through 10 kDa nominal MWCO centrifugal concentrators. Zebrafish embryos/larvae were then exposed to either the (nano)particulate fraction (i.e., retentate) or the dissolved fraction (i.e., filtrate) and assessed for mortality and morphological endpoints of toxicity.

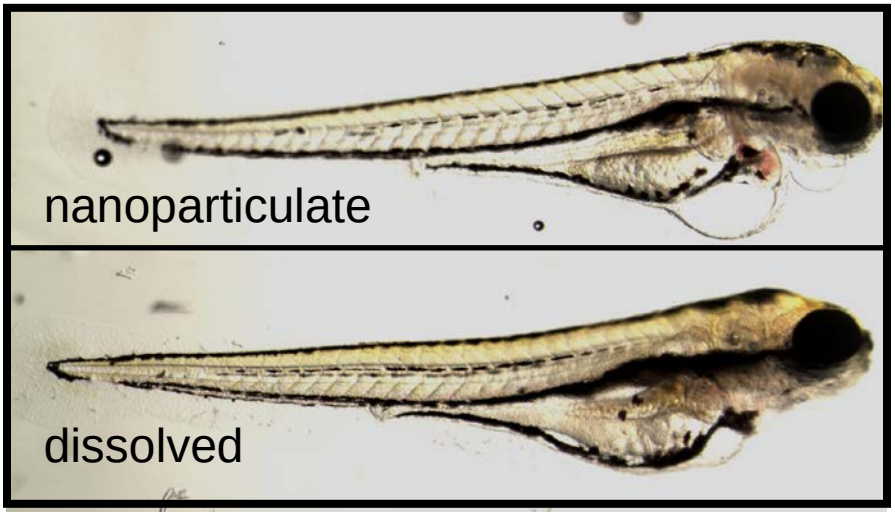

Figure S2. Representative micrographs of larvae at 120 hpf after exposure to the (nano)particulate or dissolved fraction of weathered QDs. Larvae exposed to either fraction exhibited several morphological endpoints of toxicity; however, those resulting from exposed to the (nano)particulate fraction appeared more severe.

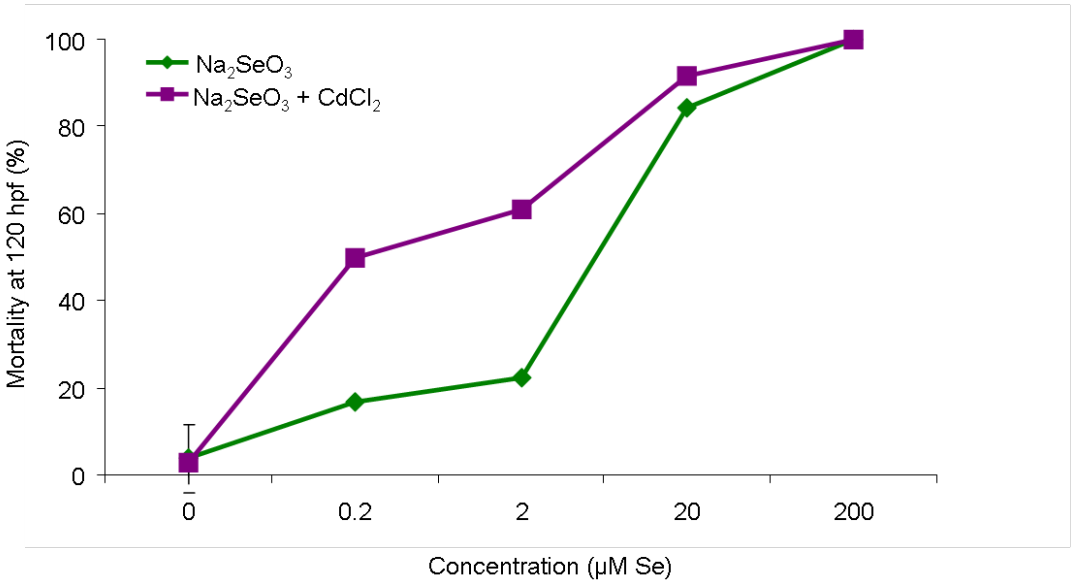

Figure S3. Co-exposures to Cd^{2+} + SeO_3^{2-} resulted in increased toxicity to zebrafish larvae relative to exposure to SeO_3^{2-} alone. Embryos/larvae were exposed to sodium selenite (Na_2SeO_3) alone or in conjunction with $CdCl_2$ at a constant 1:1 Se-to-Cd ratio, and mortality was recorded at 120 hpf. Mortality was increased in larvae co-exposed to $CdCl_2$ and Na_2SeO_3 (denoted by the left shift in the dose-response curve). Calculated LC_{50} values were 5.1 ($CI_{95\%}$: 3.7-7.1) and 0.27 ($CI_{95\%}$: 0.03-2) µM Se for SeO_3^{2-} alone and SeO_3^{2-} + Cd^{2+}, respectively. Data are means ± SE of at least duplicate experiments. In some cases, error bars are smaller than the size of the symbols.

Table S1. Concentrations (µM) of Cd, Se and Zn in weathered QD solutions[a]

element	total	(nano)particulate		dissolved	
	(µM)	(µM)	(%)	(µM)	(%)
cadmium	25 ± 0.8	4.2 ± 0.29	19 ± 1.3	17.2 ± 0.52	70 ± 3.1
selenium	24 ± 2.7	6.0 ± 0.56	25 ± 3.6	18.3 ± 0.61	76 ± 8.9
zinc	0.6 ± 0.43	0.0 ± 0.02	0 ± 0.0	0.23 ± 0.02	40 ± 26

[a] Weathered QDs suspensions (20 µM Cd equivalents) were filtered through centrifugal concentrators with nominal molecular weight cutoff of 10 kDa (pore size ~2.8 nm).[1] The concentrations of Cd, Zn and Se were measured in the retentate and filtrate. Concentrations of Cd and Zn were determined by ICP-OES and were reported in ref. *1*. Selenium concentrations were measured by ICP-MS. The fraction retained (i.e., retentate) by the filter is operationally defined here as (nano)particulate, while the fraction which passed through the filter (i.e., filtrate) is considered dissolved. Recoveries of Cd and Zn were less than 100% indicating some loss of these metals to the regenerated cellulose membrane.

References

1. Metz, K.M.; Magham, A.N.; Bierman, M.J.; Jin, S.; Hamers, R.J.; Pedersen, J.A. Engineered nanomaterial transformation under oxidative environmental conditions: Development of an *in vitro* biomimetic assay. *Environ. Sci. Technol.* **2009**, *43*, 1598-1604.