EPA Public Access

Author manuscript

Environ Sci Technol. Author manuscript; available in PMC 2018 August 30.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Sci Technol. 2017 February 07; 51(3): 1357–1363. doi:10.1021/acs.est.6b04475.

Aggregation, sedimentation, dissolution and bioavailability of quantum dots in estuarine systems

Yao Xiao^{a,^}, Kay T. Ho^{*,b}, Robert M. Burgess^b, and Michaela Cashman^c

^aNational Research Council at Atlantic Ecology Division, US Environmental Protection Agency, 27 Tarzwell Dr., Narragansett, RI 02882

^bAtlantic Ecology Division, US Environmental Protection Agency, 27 Tarzwell Dr., Narragansett, RI 02882

^cUniversity of Rhode Island, Department of Geosciences, Kingston, RI 02881

Abstract

To understand their fate and transport in estuarine systems, the aggregation, sedimentation and dissolution of CdSe quantum dots (QDs) in seawater were investigated. Hydrodynamic size increased from 40–60 nm to >1 μ m within one hour in seawater, and the aggregates were highly polydisperse. Their sedimentation rates in seawater were measured to be 4–10 mm/day. Humic acid (HA), further increased their size and polydispersity, and slowed sedimentation. Light increased their dissolution and release of dissolved Cd. The ZnS shell also slowed release of Cd ions. With sufficient light, HA increased the dissolution of QDs, while with low light, HA alone did not change their dissolution. The benthic zone in estuarine systems is the most probable long-term destination of QDs due to aggregation and sedimentation. The bioavailability of was evaluated using the mysid *Americamysis bahia*. The 7-day LC50s of particulate and dissolved QDs were 290 and 23 μ g (total Cd) /L, respectively. For mysids, the acute toxicity appears to be from Cd ions; however, research on the effects of QDs should be conducted with other organisms where QDs may be lodged in critical tissues such as gills or filtering apparatus, and Cd ions may be released and delivered directly to those tissues.

Abstract

Experimental setup for dissolution experiment under natural light.

*Corresponding Author ho.kay@epa.gov 27 Tarzwell Drive Narragansett, RI 02882 phone:401 782-3196 Fax: 401 782-3030.

[^]currently at Country Garden Holding Company Limited, Suite 1702,17/F, Dina House, Ruttonjee Center, 11 Duddell St., Central, Hong Kong

Supporting Information

Additional methodology details regarding the detailed information about the QDs tested and the light filters used in dissolution experiment are located in the SI. SI figures include TEM characterization of QDs tested, graphic illustration of the dissolution experimental setup, and additional results of dissolution experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Introduction

The increasing use of engineered nanoparticles (NPs) in consumer and medical products¹ poses potential risks to humans and ecosystems^{2,3}. Their highly valuable societal benefits in drug targeting and in-vivo biomedical imaging make quantum dots (QDs) one of the most widely used engineered NPs⁴. In addition, because of their highly tune-able emission wavelengths, they are increasingly used in flat screen applications, solar cells and ink-jet printing^{5,6}. Structurally, QDs often consist of a metalloid crystalline core of a variety of metal complexes such as CdSe, ZnS and CdTe⁷, and an outer shell or coating that render them bioavailable and biocompatible depending upon the surface coating⁸. Of those varieties, CdSe/ZnS (core/shell) QDs are the most frequently utilized, because of their wide light absorbance range, narrow emission spectrum, and size dependent emission⁹⁻¹¹.

Because of this wide usage, many QDs will inevitably find their way into the estuarine system at the end of their life cycle¹². The majority of research on the fate, transport and effects of QDs have focused on freshwater systems^{13,14}. Despite the unique characteristics of estuarine systems¹⁵, such as elevated salinity, the environmental fate of QDs in estuarine settings has been relatively understudied. Because of the elevated salinity, QDs are expected

to rapidly aggregate and precipitate upon entering marine systems; polymeric surface coatings¹⁶ and abundant dissolved and colloidal natural organic matter (NOM), such as humic substances¹⁷, however, may limit the aggregation behavior of QDs in seawater. For example, the repulsive steric interaction between polymeric surface coatings or NOM may result in less aggregation and increased stabilization of nanoparticles in solution keeping them available for transport and, possibly, bioavailable to aquatic water column organisms depending upon the surface coating. Despite the effects of polymeric surface coatings and NOMs, accumulation in estuarine sediment may be the ultimate fate for many QDs¹⁸, as a result of aggregation and sedimentation in seawater. However, very few toxicity studies of QDs have been performed on estuarine benthic organisms¹⁹. Thus, the aggregation and sedimentation of QDs in estuarine systems in the presence of polymeric coatings and NOM needs further investigation, especially considering that QDs will end up in estuaries.

QDs may undergo a variety of transformations in estuarine systems that will impact their transport, fate and effects. One relevant process to their bioavailability is dissolution. Numerous studies have suggested that metal ions (e.g., Cd²⁺) resulting from the dissolution of QDs contribute to overall aquatic toxicity^{20, 21}. This behavior has been observed for other metallic NPs²². However, in the case of cadmium QDs, there are discrepancies in the literature on whether the intact QD core^{23, 24} or the cadmium ions are more toxic; therefore, studying the dissolution of QDs is crucial for understanding their bioavailability and potential toxicity.

Given these uncertainties, this research investigated the aggregation, sedimentation and dissolution of CdSe QDs in seawater in an effort to better understand their transport behavior and fate in estuarine systems. In addition, an evaluation of the bioavailability of CdSe QDs and their metal constituents in estuarine waters was performed. CdSe QD bioavailability was indicated based on the presence of toxicity to the mysid *Americamysis bahia* (mysid), a commonly used model epibenthic organism. These are the first toxicity data for CdSe QDs using an estuarine epibenthic crustacean species²⁵.

Materials and Methods

Chemicals.

Three types of QDs were purchased from Ocean NanoTech (San Diego CA, USA): CdSe/ZnS QDs with carboxylic acid (CdSe-COOH), CdSe/ZnS QDs with a positively charged polydiallyldimethylammonium (PDDA) surface (CdSe-PDDA), and CdSe water soluble QDs without the ZnS shell (CdSe-NS). Detailed information about QDs used in this paper is provided in Table S1. Their emission peak wavelength is 580 nm, the full width of half maximum is less than 35 nm, and they were dispersed in deionized (DI) water. All three types of QDs contain a CdSe core and organic coatings. CdSe-COOH was coated with a monolayer of oleic acid/octadecylamine and a monolayer of amphiphilic polymer rich in carboxylic acid. CdSe-PDDA had a mercaptopropionic acid coating. CdSe-NS, without the ZnS shell, contained a mercaptopropionic acid coating. Both CdSe-PDDA and CdSe-NS are used for solar cell fabrication, and CdSe-COOH is used for biomedical applications due to its capability to conjugate with proteins. QDs stock solutions were prepared by diluting the original QDs solution in 74.5 mg/L of potassium chloride solution, sonicating in a bath

sonicator, filtering through a 200-nm Millipore PTFE filter, and storing at 4 °C in the dark prior to use. A humic acid sodium salt was purchased from Sigma Aldrich (St. Louis MO, USA).

Characterization of QDs.

Transmission electron microscopy (TEM) was employed to determine the morphology and size of the studied QDs. At least 40 particles were used to statistically compute the mean particle size distribution via the image analysis program ImageJ. Dynamic light scattering (DLS) was utilized to measure the hydrodynamic size, size distribution, and zeta potential (Brookhaven ZetaPALS, Brookhaven Instruments Corporation, Holtsville, NY USA). TEM images, particle size distributions measured by TEM, and hydrodynamic size distributions are summarized in Table S1 and Figure S1-S3. The molar concentration of QDs in the stock solution was nominally 100 nM. The total Cd concentrations of CdSe-COOH, CdSe-PDDA and CdSe-NS in their stock solutions were 2.40 ± 0.13 , 1.88 ± 0.09 , and 1.35 ± 0.11 mg Cd/L, respectively.

Aggregation and sedimentation experiments.

The aggregation experiments were performed by mixing the QDs stock solution of CdSe-COOH and CdSe-PDDA with laboratory-prepared seawater (reconstituted seawater prepared with natural brine and diluted with deionized water to attain a salinity of 30 ‰) at 22 °C, and monitoring the change in the hydrodynamic diameter in the dark via DLS. To investigate the sedimentation of QDs, 10 mL of a QD stock solution and seawater mixture, with QD concentrations (total Cd) between 0.1 and 0.3 mg/L, was placed in a 15-mL plastic centrifuge tube and kept in the dark by wrapping the tube with aluminum foil. Samples of 0.1 mL volume were taken from the supernatant, which was defined as the water column at 50 mm below the water surface from the solution of mixed QDs and seawater over 12 d (i.e. 0, 1, 2, 3, 4, 6, 8, 10, 12 d) at 22 °C to investigate the settling of QDs. After each sample was taken, the total Cd concentration was measured via inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Horiba Jobin Yvon ICP (Kyoto, Japan), following acid digestion as described elsewhere²⁶.

Dissolution experiments under different light conditions.

Using three types of QDs, stock solution was diluted in laboratory prepared seawater (salinity = 30 ‰) and placed in duplicate plastic Corning cell culture flasks. The total volume was 100 mL and the total Cd concentration of each type of QD was approximately 0.5 mg/L. The flasks were then placed in a continuously flowing natural seawater bath located outdoors to use natural sunlight, maintained at 6°C, and covered with a transparent plexiglass cover (Fig S4). The cover was divided into three regions: the first had no additional light filter, the second had one layer of light filtering material, and the third had two layers of light filtering material. The light filtering material used in this study was Supergel #374 Sea Green (Rosco, Stamford CT, USA), which is a widely used plastic color filter with a 3-mm thickness. This color filter attenuates the natural sunlight in a manner similar to water (Fig S5). In this design, it was used to mimic the light conditions at different water depths. The UV intensity was measured using a UV radiometer (Model UVX-25, UVP Co.). A set of flasks was wrapped in aluminum foil as a dark control in order to

measure the background dissolution of QDs without light exposure. To investigate the effect of NOM on the dissolution of QDs in seawater, 20 mg/L of humic acid was added to half of the samples in each region of the water bath. The dissolution experiments were repeated, in parallel, in an indoor chamber, with a fluorescence lamp turned on continuously. All dissolution experiments were conducted in triplicate. At each time point (i.e., 0, 1, 2, 3, 4, 5, 9, 12, 16, 19, 23, 26, 30 d), 1 mL of sample was withdrawn from the flask. The QD nanoparticles and dissolved QD were operationally fractionated by centrifugation for 30 min at 7000× g, using an Amicon Ultra-4 centrifugal ultrafilter (Amicon Ultracel 3000 Daltons, Millipore, USA). The concentration of dissolved QDs and particulate QDs were determined by ICP-AES as described earlier.

Toxicity testing with the mysid *Americamysis bahia*.

Americamysis bahia was chosen as a standard test organism because its epibenthic nature ensures that exposure would occur from settling QD at the benthic surface. Also, as *A. bahia* is a standard test organism, there is a large data base with which to compare results. Toxicity tests with CdSe-COOH, were conducted based on methods discussed in Ho et al.²⁷. QD stock solutions were diluted in laboratory prepared seawater to obtain a series of treatments with different nominal concentrations of Cd. The QD suspensions were placed in an indoor chamber at 20°C, with a fluorescence lamp (UV intensity = 6.43 μW/cm²) on continuously for seven days, as earlier experiments confirmed that the dissolution of QDs reached equilibrium after seven days. Water samples were then removed from the water column and diluted with clean seawater to a total volume of 60 mL. The exposure concentrations of CdSe-COOH measured at the beginning of the test using ICP-AES, expressed as total Cd, were between 0.06 and 1.7 mg/L. Ten 48 h old laboratory-cultured mysids were added into each of three replicate exposure chambers per QD concentration treatment, and fed *ad lib.* with brine shrimp, *Artemia salina*, daily. The fluorescence light cycle was 16:8 light:dark cycle, and each exposure chamber was gently aerated. Surviving mysids were visually enumerated at 48 and 96 hours and at 7 days when the experiment was terminated. Missing mysids were considered mortalities. The LC50 was calculated using the inhibition program ICPIN²⁸.

Results and Discussion

Aggregation of QDs and the effect of HA.

The behavior of the hydrodynamic diameter of CdSe-COOH and CdSe-PDDA in the stock solutions (i.e. 0.75 g/L of KCl), water with different salinities, and HA treatments were monitored by DLS (Figure 1 a and b). The sizes of both QDs were relatively stable in the stock solution at a diameter of approximately 20 nm over the duration of the experiments. In full strength seawater (salinity = 30 ‰), both QDs quickly aggregated and within one hour, reached an equilibrium size of more than 1 μm with polydispersity index (PDI) larger than 0.9. (Aggregates with PDI > 0.4 are generally considered polydispersed.) In comparison, in a lower salinity environment (i.e., salinity = 1 ‰), the aggregation of both QDs was much slower and the equilibrium sizes of QD aggregates and PDI were much smaller (~ 500 nm and ~0.4). As diffusion-limited aggregation usually leads to aggregates that are highly poly-

dispersed²⁹, the PDI index is additional evidence that the aggregation of QDs in seawater was diffusion limited.

In terms of aggregation kinetics and size, CdSe-COOH and CdSe-PDDA were similar indicating that in an aquatic environment with ionic strength as high as seawater, the surface coatings played a limited role in determining the aggregation behavior.

In the presence of HA, the aggregate size of CdSe-PDDA was increased by approximately 70%; however, HA increased the size of the CdSe-COOH aggregates by only about 10%. In seawater, the hydrodynamic diameter of HA aggregates (without any QD in the system) was measured to be around 300 nm. The reason for this difference in aggregation behavior between CdSe-COOH and CdSe-PDDA may result from differences in surface charge. Due to the extremely compressed electrical double layer (EDL) in seawater¹⁷, the surface coatings of QDs could extend out of the EDL and interact with HA. In this scenario, HA served as a bridging agent because of the electrostatic attraction between the negatively charged HA and positively charged CdSe-PDDA. In contrast, the negative charge associated with CdSe-COOH would not undergo the same intermolecular interaction with the HA. Therefore, HA increased the aggregate size of CdSe-PDDA, while CdSe-COOH aggregates were not as substantially affected. The observed difference between the two coatings of the QD in the presence of HA supports the hypothesis that bridging may play a role in aggregation.

Sedimentation of QDs in seawater and the effect of NOM.

A semi-empirical model was borrowed from Quik et al. (2013)³⁰ to interpret the sedimentation data, by describing the concentration of QDs (C_t [mg/L]) in the supernatant as a function of time:

$$C_t = (C_0 - C_{NS})e^{-\left(\frac{V_s}{h} + k_D\right)t} + C_{NS} \quad (1)$$

In this equation, C_0 (mg/L) is the concentration of QDs (i.e. total Cd) at the beginning of the experiment; C_{NS} (mg/L) is the QD concentration after it reached equilibrium with the QD remaining in the supernatant considered as not settling; V_s (mm/d) is the sedimentation rate; h (mm) is the sedimentation length, which is measured from the water surface to the measurement depth and is 50 mm in this experimental setup; k_D (d⁻¹) is the dissolution rate, which is considered to be zero, as a separate experiment showed that the dissolution of QDs in the dark was minimal (Figure 2), and t is the elapsed time in days (d).

The sedimentation experiment results are summarized in Table 1 with results fitting the above model ($r^2 > 0.98$). In the presence of HA, more QDs remained in the supernatant rather than settling, which might be attributed to the relatively low density structure of QD-HA aggregates.

The sedimentation rates of CdSe-COOH and CdSe-PDDA in seawater were around 10 mm/d. Compared to the sedimentation rates of other nanoparticles reported elsewhere³⁰,

both QDs settled 2–3 times more quickly than nanoparticles such as CeO₂, SiO₂-Ag and PVP-Ag in seawater, and 3–10 times more quickly than those nanoparticles in fresh water. The introduction of HA slowed down the sedimentation of both QDs; however, the sedimentation rate of CdSe-PDDA decreased by 48% compared to 16% that of CdSe-COOH, which might be explained by the larger size and less dense structure of the CdSe-PDDA-HA aggregates discussed above.

Dissolution of QDs in seawater and the effect of light conditions and NOM.

As shown in Figure 2, the light filters decreased the dissolution of CdSe-COOH (i.e., shown as the ratio of dissolved Cd versus total Cd on the y-axis) in seawater. Without the light filter, approximately 27% of QDs dissolved under sunlight. One layer of light filtering material decreased the dissolution rate by more than a half, while two layers of light filtering material appeared to have the same effect as one layer, and no apparent dissolution was observed under completely dark condition. Similar results were observed for CdSe-PDDA and CdSe-NS (Fig S6 and S7). These data indicate that photo-oxidation contributes to QDs dissolution in seawater¹⁶. The UV intensity of 100% transmitted light and UV intensity under one layer and two layers of light filtration were measured to be 195.7, 14.12 and 8.97 $\mu\text{W}/\text{cm}^2$, respectively. The plexiglass cover and the plastic culture flasks accounted for about 75% of UV attenuation, as the direct measurement of UV intensity under the sun was around 800 $\mu\text{W}/\text{cm}^2$. Based on previous reports³¹, no light filtration, one layer of filtration, and two layers of light filtration produced similar UV intensities as light at the depths of approximately 0.8, 2.5 and 2.8 m, respectively, for coastal waters with natural turbidity, and 27, 78 and 88 m for the open ocean, respectively. Moreover, the sunlight rarely reaches past 5 m in turbid coastal waters or 150 m in open ocean, where the conditions can be considered as “dark”. As noted, these data indicate that there was minimal dissolution of QDs in the dark.

The effects of shell and surface coatings on dissolution are illustrated in Figure 3. The dissolution rate of CdSe-NS was higher than that of either CdSe-COOH or CdSe-PDDA, which suggested that the ZnS shell played a crucial role in preventing the QDs from dissolving. Since photo-oxidation is a factor in the breakdown of QDs, the ZnS shell might serve as a barrier to limit the exposure of the CdSe core to oxidative species (e.g. free radicals). In addition, it was observed that dissolution of QDs in seawater was slower than compared to freshwater (Fig. S8). This may have occurred because the larger aggregates in seawater led to smaller specific surface area, or the increased ions in seawater may have decreased the dissolution rate. Between CdSe-COOH and CdSe-PDDA, there was no significant difference in dissolution rates, possibly because they had the same CdSe-core-ZnS-shell structure.

The effect of NOM on QD dissolution depended on the light condition, as shown in Figure 4(a). When the light condition was favorable for QD dissolution, the presence of HA increased the dissolution rate of CdSe-COOH; however, when light was limited, the dissolution rate did not change with the presence of HA. This observation further supports the hypothesis put forward by Zhang et al.¹⁷ that the dissolution of QDs was caused by the generation of reactive oxygen species (ROS) by HA aided by enhanced light intensity.

Another aspect of the effect of NOM on QD dissolution was that NOM might change the hydrodynamic size of QD aggregates as shown previously (Figure 1) with larger aggregate sizes often corresponding with decreased dissolution. It appears that light intensity is a more important factor in QD dissolution than the presence of HA.

The presence of HA also had different effects on the dissolution of QDs with different surface coatings (Figure 4b). The presence of HA enhanced the dissolution of CdSe-COOH; while the dissolution rate of CdSe-PDDA was not observed to change. A possible explanation for this difference might be the self-quenching of ROS by a putative CdSe-PDDA-HA aggregate. As discussed above in the section on QD aggregation, we suspect that the CdSe-PDDA forms a bridge with the HA that reduces the dissolution effects of light intensity. As the CdSe-COOH is unable to form such a bridge because of its negative charge, it is more vulnerable to dissolution resulting from exposure to light.

Bioavailability and toxicity of QDs to the mysid *Americamysis bahia*.

Control survival of *A. bahia* was 97% for the 7-day exposure. As the concentration of QDs increased, survival gradually declined. Samples with higher QD concentrations (i.e. total Cd 780 µg/L) had 100% mortality after 96 hours (Figure 5a and b).

As mysid survival results for 96 h and 7 d were very similar, the data were combined in Figure 5. The LC50s for particulate CdSe-COOH and dissolved Cd after 7 days were 290 and 23 µg/L, respectively (Table 2). Voyer and Modica³² reported that *A. bahia*'s LC50 for dissolved cadmium ranged from approximately 33 to 82 µg/L. Our LC50 of 23 µg/L for dissolved Cd is similar to this range. Effect LC50 concentrations for Cd QD in the literature range from 10 µg to 100 mg/L, depending upon the type of Cd quantum dot, the organism and endpoint measured^{33–35}. Our QD LC50 (290 µg/L) fell within this wide range of effect concentrations. Given this four order of magnitude range of reported effects, it is difficult to make generalizations about the toxicity of Cd QD, except that a number of researchers have found that the shell around the Cd core seems to afford some protection to organisms from the toxic Cd ions by slowing down Cd dissolution^{36–38}. In our exposures we also found that the CdSe-COOH QDs were less toxic than dissolved Cd. In addition, there appear to be different metabolic uptake pathways between dissolved Cd and particulate Cd in the QDs^{39–41}. It should be noted that our LC50 measures and experimental design take into account a realistic and aged exposure of particulate and dissolved quantum dots. Research on QDs and different types of nanoparticles has shown that the direct uptake of nanoparticles such as CeO₂⁴² and TiO₂ by sediment dwelling species⁴³ can result in toxicity, and that the nanoparticle form taken up by organisms have a different mode of action than the dissolved form^{39–41, 44, 45}. The particulate nature of the QD may play a role in delivering toxic Cd ions directly to tissues such as gills or filtering apparatus if the particle becomes lodged in tissues. More research needs to be performed on the bioavailability of cadmium based QDs in order to determine their uptake, bioaccumulation, and toxic modes of action in marine organisms.

Finally, zinc is a component of the outer shell of both of these QDs and, like cadmium; it may undergo dissolution in seawater. Furthermore, zinc is known to cause toxicity to marine organisms (<https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic->

life-criteria-table); however, the 96-h LC50 of zinc to this mysid is approximately 500 µg/l⁴⁶, indicating it is far less toxic than cadmium⁴⁷ and is probably not the major source of risk resulting from QDs in the marine environment. In addition, as previously reported above^{34–36} the shell surrounding the Cd core appears to give some protection to organisms from toxicity.

Environmental Implications

With the incorporation of QDs in light emitting diode (LED) displays, the use of quantum dots in electronics is on the exponential rise. Environmental concentrations while unknown, will certainly increase with increased usage. In order to understand the long-term fate and potential effects of QDs in estuarine environments, we must investigate how the intrinsic complexity of the composition and size of QD themselves as well as the polydispersity of the QD aggregates are affected by the multiple environmental factors present in estuaries system. This investigation examined three types of cadmium QDs and looked at two predominant estuarine factors: salinity and NOM concentration. The high salinity of seawater created an environment in which QDs readily aggregated at an accelerated rate. However, the rapid aggregation also led to a loosely-arranged and less dense structure that slowed precipitation especially in the case of the CdSe-PDDA QDs. The inclusion of NOM further increased the aggregate size, while making the aggregate structure even less dense.

Despite the processes that reduce the rate of precipitation, it is assumed that the benthos is the most likely long-term destination of QDs, especially in estuaries; however, the time it takes for the QDs to reach the benthos is longer than expected. With the caveat that this laboratory derived settling time (10mm/day) does not take into account other environmental processes like resuspension and horizontal transport, this longer settling time suggests that in an average 10 m deep coastal estuary, the settling time would be 1000 days or over 2 years. This prolonged exposure in the water column could certainly be sufficient time to cause toxicity to water column organisms via dissolution of cadmium, or by QD particles entering the gills or filtering apparatus of those organisms. The effects of these other environmental factors on the settling rate still needs to be determined by further research.

The ability of estuarine systems to slow the dissolution of QDs is greater than in fresh waters because of two contributing factors. Firstly, QDs form large aggregates in seawater, thus reducing the exposed surface area and hampering dissolution of the cadmium. Secondly, most regions in the ocean, especially in estuaries, can be considered as “dark”, thus light penetration is attenuated and photo-oxidation of QDs is limited. In addition, interactions with bacteria or phytoplankton may also make the QDs agglomerations denser and prone to settling. The situation would certainly be dynamic but given that dissolution is almost negligible in the dark, we believe the particles would eventually settle to the benthos. As a result, most QDs will likely reach the sediment in particulate form. Many previous studies point out that the toxicity of cadmium-based QDs is mainly due to the release of cadmium ions^{48–50}. Since benthic organisms are likely to encounter particulate QDs rather than cadmium ions, it is worthwhile to further investigate the toxicity of QD particles in benthic environments.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

This research was performed while the author held a National Research Council Research Associateship Award at US EPA Atlantic Ecology Division. We thank Drs. A. Parks, M. Pelletier and M. Cantwell for experimental assistance and Drs. T. Luxton, W. Boothman and A. Parks for technical review. This is EPA contribution number AED-016351 of the US Environmental Protection Agency (EPA), Atlantic Ecology Division (AED) and has been technically reviewed by AED; however, it does not necessarily represent the views of the USEPA. No official endorsement of any aforementioned product should be inferred.

References

1. Wiesner MR; Lowry GV; Alvarez P; Dionysiou D; Biswas P, Assessing the risks of manufactured nanomaterials. *Environ. Sci. Technol.* 2006, 40, 4337–4345.
2. Marambio-Jones C; Hoek EMV, A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *J. Nanopart. Res.* 2010, 12, 1531–1551.
3. Fabrega J; Luoma SN; Tyler CR; Galloway TS; Lead JR, Silver nanoparticles: Behaviour and effects in the aquatic environment. *Environ. Int.* 2011, 37, 517–531. [PubMed: 21159383]
4. Hardman R, A toxicologic review of quantum dots: Toxicity depends on physicochemical and environmental factors. *Environ. Health Perspective* 2006, 114, 165–172.
5. Shirasaki Y; Supran GJ; Bawendi MG; Bulovic V, Emergence of colloidal quantum-dot light-emitting technologies. *Nat. Photonics* 2013, 7, 13–23.
6. Jamieson T; Bakhshi R; Petrova D; Pocock R; Imani M; Seiflian AM, Biological applications of quantum dots. *Biomaterials* 2007, 28, 4717–4732. [PubMed: 17686516]
7. Werlin R; Priester JH; Mielke RE; Kramer S; Jackson S; Stoimenov PK; Stucky GD; Cherr GN; Orias E; Holden PA, Biomagnification of cadmium selenide quantum dots in a simple experimental microbial food chain. *Nat. Nanotechnol.* 2010, 6, 65–71. [PubMed: 21170041]
8. Domingos RF; Simon DF; Hauser C; Wilkinson KJ, Bioaccumulation and effects of CdTe/CdS quantum dots on *Chlamydomonas reinhardtii* nanoparticles or the free ions? *Environ. Sci. Technol.* 2011, 45, 7664–7669. [PubMed: 21842898]
9. Nga PT; Chinh VD; Hanh VTH; Nghia NX; Dzong PT; Barthou C; Benalloul P; Laverdant J; Maitre A, Optical properties of normal and ‘giant’ multishell CdSe quantum dots for potential application in material science. *Int. J. Nanotechnol.* 2011, 8, 347–359.
10. Michalet X; Pinaud FF; Bentolila LA; Tsay JM; Doose S; Li JJ; Sundaresan G; Wu AM; Gambhir SS; Weiss S, Quantum dots for live cells, in vivo imaging, and diagnostics. *Science* 2005, 307, 538–544. [PubMed: 15681376]
11. Sark W. G.v.; Frederix PLTM.; Heuvel D. J. V. d.; Gerritsen HC.; Bol AA; Lingen J. N. J. v.; Donega C. d. M.; Meijerink A., Photooxidation and photobleaching of single CdSe/ZnS quantum dots probed by room-temperature time-resolved spectroscopy. *J. Phy. Chem. B* 2001, 105, 8281–8284.
12. Matraga V; Corsi I, Toxic effects of engineered nanoparticles in the marine environment: Model organisms and molecular approaches. *Marine Environ. Research* 2012, 76, 32–40.
13. Torkzaban S; Bradford SA; Wan J; Tokunaga T; Masoudih A, Release of quantum dot nanoparticles in porous media: Role of cation exchange and aging time. *Environ. Sci. Technol.* 2013, 47, 11528–11536. [PubMed: 24041419]
14. Quevedo IR; Tufenkji N, Mobility of functionalized quantum dots and a model polystyrene nanoparticles in saturated quartz sand and loamy sand. *Environ. Sci. Technol.* 2012, 46, 4449–4457. [PubMed: 22423631]

15. Klaine SJ; Alvarez PJJ; Batley GE; Fernandes TF; handy RD; Lyon DY; Mahendra S; McLaughlin MJ; Lead JR, Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environ. Toxicol. Chem.* 2008, 27, 1825–1851. [PubMed: 19086204]
16. Li Y; Zhang W; Li K; Yao Y; Niu J; Chen Y, Oxidative dissolution of polymer-coated CdSe/ZnS quantum dots under UV irradiation: Mechanisms and kinetics. *Environ. Pollution* 2012, 164, 259–266.
17. Zhang S; Jiang Y; Chen C; Spurgin J; Schwehr KA; Quigg A; Chin W; Santschi PH, Aggregation, dissolution and stability of quantum dots in marine environments: Importance of extracellular polymeric substances. *Environ. Sci. Technol.* 2012, 46, 8764–8772. [PubMed: 22834414]
18. Quick JTK; Stuart MC; Wouterse M; Peijnenburg W; Hendriks AJ; Meent D. v. d., Natural colloids are the dominant factor in the sedimentation of nanoparticles. *Environ. Toxicol. Chem.* 2012, 31, 1019–1022. [PubMed: 22447393]
19. Rocha TL; Gomes T; Mestre NC; Cardoso C; Bebianno MJ, Tissue specific responses to cadmium-based quantum dots in the marine mussel *Mytilus galloprovincialis*. *Aqua. Toxicol.* 2015, 169, 10–18.
20. Mahendra S; Zhu H; Colvin VL; Alvarez PJJ, Quantum dot weathering results in microbial toxicity. *Environ. Sci. Technol.* 2008, 42, 9424–9430. [PubMed: 19174926]
21. Pace HE; Leshner EK; Ranville JF, Influence of stability on the acute toxicity of CdSe/ZnS nanocrystals to *Daphnia Magna*. *Environ. Toxicol. Chem.* 2010, 29, 1338–1344. [PubMed: 20821577]
22. Angel BM; Batley GE; Jarolimek CV; Rogers NJ, The impact of size on the fate and toxicity of nanoparticulate silver in aquatic systems. *Chemosphere* 2013, 93, 359–365. [PubMed: 23732009]
23. King-Heiden TC; Wicinski PN; Mangham AN; Metz KM; Nesbit D; Pedersen JA; Hamers RJ; Heideman W; Peterson RE, Quantum Dot Nanotoxicity Assessment Using the Zebrafish Embryo. *Environ. Sci. Technol.* 2009, 43, 1605–1611. [PubMed: 19350942]
24. Priester JH; Stoimenov PK; Mielke RE; Webb SM; Ehrhardt C; Zhang JP; Stucky GD; Holden PA, Effects of soluble cadmium salts versus CdSe quantum dots on the growth of planktonic *Pseudomonas aeruginosa*. *Environ. Sci. Technol.* 2009, 43, 2589–2594. [PubMed: 19452921]
25. Rocha TL; Mestre NC; Sabóia-Morais SMT.; Bebianno MJ., Environmental behaviour and ecotoxicity of quantum dots at various trophic levels: A review. *Environ. Int.* 2017, 98, 1–17. [PubMed: 27745949]
26. Zhang W; Yao Y; Chen YS, Imaging and quantifying the morphology and nanoelectrical properties of quantum dot nanoparticles interacting with DNA. *J. Phy. Chem. C* 2011, 115, 599–606.
27. Ho KT; Kuhn A; Pelletier M; McGee F; Burgess RM; Serbst J, Sediment toxicity assessment: Comparison of standard and new testing designs. *Arch. Environ. Contam. Toxicol.* 2000, 39, 462–468. [PubMed: 11031306]
28. Norberg-King TJ A linear interpolation method for sublethal toxicity: the inhibition concentration (ICp) approach, 2.0; U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN, 1993.
29. Zhou Y; Antonietti M, Synthesis of Very Small TiO₂ Nanocrystals in a Room-Temperature Ionic Liquid and Their Self-Assembly toward Mesoporous Spherical Aggregates. *Journal of the American Chemical Society* 2003, 125, (49), 14960–14961. [PubMed: 14653710]
30. Quik JTK; Velzeboer I; Wouterse M; Koelmans AA; Meent D. v. d., Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Wat. Res.* 2013, 48, 269–279.
31. Johannessen SC; Miller WL; Cullen JJ, Calculation of UV attenuation and colored dissolved organic matter absorption spectra from measurement of ocean color. *J. Geophys. Res. Atmosph.* 2003, 108, 223–250.
32. Voyer RA; Modica G, Influence of salinity and temperature on acute toxicity of cadmium to *Mysidopsis bahia molenock*. *Arch. Environ. Contam. Toxicol.* 1990, 19, 124–131. [PubMed: 2331146]
33. Gagne F; Auclair J; Turcotte P; Fournier M; Gagnon C; Sauve S; Blaise C, Ecotoxicity of CdTe quantum dots to freshwater mussels: Impacts on immune system, oxidative stress and genotoxicity. *Aquatic Toxicology* 2008, 86, (3), 333–340. [PubMed: 18160110]

34. Katsumiti A; Gilliland D; Arostegui I; Cajaraville MP, Cytotoxicity and cellular mechanisms involved in the toxicity of cds quantum dots in hemocytes and gill cells of the mussel *mytilus galloprovincialis*. *Aquatic Toxicology*, (0).
35. Buffet P-E; Zalouk-Vergnoux A; Poirier L; Lopes C; Risso-de Faverney C; Guibbolini M; Gilliland D; Perrein-Ettajani H; Valsami-Jones E; Mouneyrac C, Cadmium sulfide quantum dots induce oxydative-stress and behavioural impairments in the marine clam *Scrobicularia plana*. *Environmental Toxicology and Chemistry* 2015, n/a-n/a.
36. Marmiroli M; Pagano L; Savo Sardaro ML; Villani M; Marmiroli N, Genome-Wide Approach in *Arabidopsis thaliana* to Assess the Toxicity of Cadmium Sulfide Quantum Dots. *Environmental Science & Technology* 2014, 48, (10), 5902–5909. [PubMed: 24673199]
37. Mei J; Yang L-Y; Lai L; Xu Z-Q; Wang C; Zhao J; Jin J-C; Jiang F-L; Liu Y, The interactions between CdSe quantum dots and yeast *Saccharomyces cerevisiae*: Adhesion of quantum dots to the cell surface and the protection effect of ZnS shell. *Chemosphere* 2014, 112, (0), 92–99. [PubMed: 25048893]
38. Contreras EQ; Cho M; Zhu H; Puppala HL; Escalera G; Zhong W; Colvin VL, Toxicity of Quantum Dots and Cadmium Salt to *Caenorhabditis elegans* after Multigenerational Exposure. *Environmental Science & Technology* 2012, 47, (2), 1148–1154. [PubMed: 23241207]
39. Rocha TL; Gomes T; Cardoso C; Letendre J; Pinheiro JP; Sousa VS; Teixeira MR; Bebianno MJ, Immunocytotoxicity, cytogenotoxicity and genotoxicity of cadmium-based quantum dots in the marine mussel *Mytilus galloprovincialis*. *Marine Environmental Research* 2014, 101, (0), 29–37. [PubMed: 25164019]
40. Rocha TL; Gomes T; Pinheiro JP; Sousa VS; Nunes LM; Teixeira MR; Bebianno MJ, Toxicokinetics and tissue distribution of cadmium-based Quantum Dots in the marine mussel *Mytilus galloprovincialis*. *Environ. Poll.* 2015, 204, (0), 207–214.
41. Stewart DTR; Noguera-Oviedo K; Lee V; Banerjee S; Watson DF; Aga DS, Quantum dots exhibit less bioaccumulation than free cadmium and selenium in the earthworm *Eisenia andrei*. *Environmental Toxicology and Chemistry* 2013, 32, (6), 1288–1294. [PubMed: 23417745]
42. Montes MO; Hanna SK; Lenihan HS; Keller AA, Uptake, accumulation, and biotransformation of metal oxide nanoparticles by a marine suspension-feeder. *J. Haz. Mat.* 2012, 225–226, 139–145.
43. Galloway T; Lewis C; Dolciotti I; Johnston BD; Moger J; Regoli F, Sublethal toxicity of nano-titanium dioxide and carbon nanotubes in a sediment dwelling marine polychaete. *Environ. Pollution* 2010, 158, 1748–1755.
44. Garcia-Alonso M; Rodriguez-Sanchez N; Misra SK; Valsami-Jones E; Croteau M-N; Luoma SN; Rainbow PS, Toxicity and accumulation of silver nanoparticles during development of the marine polychaete *Platynereis dumerilii*. *Sci. Total Environ.* 2014, 476–477, 688–695.
45. Wang H; Ho KT; Scheckel KG; Wu F; Cantwell MG; Katz DR; Horowitz DB; Boothman WS; Burgess RM, Toxicity, Bioaccumulation, and Biotransformation of Silver Nanoparticles in Marine Organisms. 2014.
46. Lussier SM; Gentile JH; Walker J, Acute and chronic effects of heavy metals and cyanide on *Mysidopsis bahia* (crustacea:mysidacea). *Aquatic Toxicology* 1985, 7, (1), 25–35.
47. Environmental US Protection Agency *Ambient Water Quality Criteria for Cadmium*; EPA 440/5–84-032; Office of Water US Environmental Protection Agency: Washington, DC, 1, 1985.
48. Wicinski PN; Metz KM; Heiden TCK; Louis KM; Mangham AN; Hamers RJ; Heideman W; Peterson RE; Pedersen JA, Toxicity of oxidatively degraded quantum dots to developing Zebrafish (*Danio rerio*). *Environ. Sci. Technol.* 2013, 47, 9132–9139. [PubMed: 23815598]
49. Heiden TCK; Wicinski PN; Mangham AN; Metz KM; Nesbit D; Pedersen JA; Hamers RJ; Heideman W; Peterson RE, Quantum dot nanotoxicity assessment using the zebrafish embryo. *Environ. Sci. Technol.* 2009, 43, 1605–1611. [PubMed: 19350942]
50. Mahendra S; Zhu H; Colvin VL; Alvarez PJ, Quantum dot weathering results in microbial toxicity. *Environ. Sci. Technol.* 2008, 42, 9424–9430. [PubMed: 19174926]

(a)

(b)

Figure 1.

Aggregation of (a) CdSe-COOH QD and (b) CdSe-PDDA QD in seawater and the effect of humic acid. Error bars mean standard error.

Figure 2. Dissolution kinetics of CdSe-COOH in seawater under different light conditions. Error bars mean standard error.

Figure 3. Dissolution kinetics of QDs with different shell or surface coatings in seawater under non-filtered light conditions. Error bars are the standard error.

(a)

(b)

Figure 4.

Effect of humic acid on the dissolution kinetics of QDs: (a) the effect of both light condition and HA on CdSe-COOH dissolution and; (b) the effect of both surface coatings (i.e., -COOH and -PDDA) and HA. Error bars mean standard error.

(a) **(b)** **Figure 5.**

The toxicity of (a) dissolved cadmium and (b) CdSe-COOH nanoparticle. Error bars are standard error.

Table 1.

Sedimentation of CdSe-COOH and CdSe-PDDA in seawater and the effect of HA. V_s (mm/d) is the sedimentation rate, C_0 (mg/L) is the concentration of QDs (i.e. total Cd) at the beginning of the experiment; C_{NS} (mg/L) is the QD concentration after it reached equilibrium with the QD remaining in the supernatant considered as not settling.

QDs	CdSe-COOH		CdSe-PDDA	
	w/o HA	w/HA	w/o HA	w/HA
V_s (mm/d)	10.27	8.63	8.98	4.66
C_0 (mg/L)	0.24	0.24	0.19	0.19
C_{NS} (mg/L)	0.13	0.15	0.11	0.15

Table 2.

The LC50s of dissolved cadmium and CdSe-COOH nanoparticle.

Time (h)	LC50 (µg/L)		
	CdSe-COOH NP	Dissolved Cd	Dissolved Cd (Voyer and Modica, 1990)
48	740	57	N/A
96	290	23	33~82
168	290	23	N/A