

APPENDIX A: ELECTRONIC SUPPLEMENTARY INFORMATION

for

Separation and quantification of quantum dots and dissolved metal cations by size exclusion chromatography-ICP-MS

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This supplementary information file contains content in the form of 3 tables and 5 figures. The table include ICP-MS instrument settings for two different modes of operation and measured concentrations and recoveries for some experiments. The figures include additional chromatograms obtained by SEC-ICP-MS and kinetic modeling.

Table S1. Typical ICP-MS instrument parameters for operation in conventional mode and with size exclusion chromatography.¹

Parameter	ICP-MS	SEC-ICP-MS
RF power (W)	1400	1330
Pump rate (rpm)	20	20
Auxiliary gas flow (L min ⁻¹)	1.65	1.65
Sheath gas flow ² (L min ⁻¹)	0.20	0.21
Plasma gas flow(L min ⁻¹)	16.5	18.0
Nebulizer gas flow (L min ⁻¹)	.96	1.00
Sampler Cone	Pt, 1.0 mm orifice	Pt, 1.0 mm orifice
Skimmer Cone	Pt, 0.7 mm orifice	Pt, 0.7 mm orifice
Sampling Depth (mm)	6.5	5.0
First Extraction Lens (volts)	-485	-521
Second Extraction Lens (volts)	-821	-865
Third Extraction Lens (volts)	-536	-517
Corner Lens (volts)	-728	-725
Mirror Lens Left (volts)	53	53
Mirror Lens Right (volts)	46	46
Mirror Lens Left (volts)	59	58
Entrance Lens (volts)	-1	1
Fringe Bias (volts)	-2.8	-3.0
Entrance Plate (volts)	-34	-32
Pole Bias (volts)	0.0	0.0
Scanning mode	Peak hopping	Time resolved
Readings/replicate	5	0

¹The ICPMS was optimized as needed by adjusting most of these operating parameters and ensuring the signals of test elements met the operating criteria dictated by the manufacturer. A dwell time of 10 ms was found optimal for SEC mode, and this dwell time was also used for conventional ICP-MS measurements. Note that greater sensitivity, greater precision, and lower detection limits could be achieved in ICP-MS mode with longer dwell times, e.g. 100 ms.

²Sheath gas flow refers to a fourth introduction of argon gas to the spray chamber, transfer tube, and torch system in the Bruker Aurora M90 ICP-MS. The nebulizer gas flow is introduced at the nebulizer, the sheath gas flow is introduced at the transfer tube, and the auxiliary and plasma gas flows are introduced at the torch. The role of the sheath gas flow is to allow for adjusting gas flow (and therefore aerosol velocity) to the plasma without having to adjust the nebulizer gas flow. Therefore, the nebulizing condition and the plasma condition can be optimized separately.

Table S2. Zn and Cd concentrations measured for solutions of approximately equal mass concentrations before and after centrifuge ultrafiltration and with or without 0.1 $\mu\text{g L}^{-1}$ EDTA added. Recovery of Zn and Cd was closer to 100% when EDTA was present.

	Before		After		Recovery	
	Zn	Cd	Zn	Cd	Zn	Cd
	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	(%)	(%)
no EDTA	13.1	7.5	12.9	6.9	98.4	92.2
with EDTA	16.5	10.6	16.9	10.3	102.4	96.8

Table S3. Zn and Cd concentrations measured for three suspensions of CdSe/ZnS quantum dots before and after processing with centrifuge ultrafiltration. The goal of this experiment was to check if any cations from the quantum dot stock solutions pass through the centrifuge ultrafiltration membrane. The concentrations determined before centrifugation were obtained by dissolving quantum dots with 1% nitric acid (trace metal grade), and concentrations determined after centrifugation were obtained by directly measuring the filtrate. The purchased quantum dot suspension contained some residual dissolved Zn.

	Before centrifugation		After Centrifugation	
	Zn	Cd	Zn	Cd
	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)	($\mu\text{g L}^{-1}$)
50 $\mu\text{g L}^{-1}$ QD	5.6	14.1	<DL	<DL
100 $\mu\text{g L}^{-1}$ QD	26.4	27.4	8.4	<DL
200 $\mu\text{g L}^{-1}$ QD	48.8	53.2	12.6	<DL

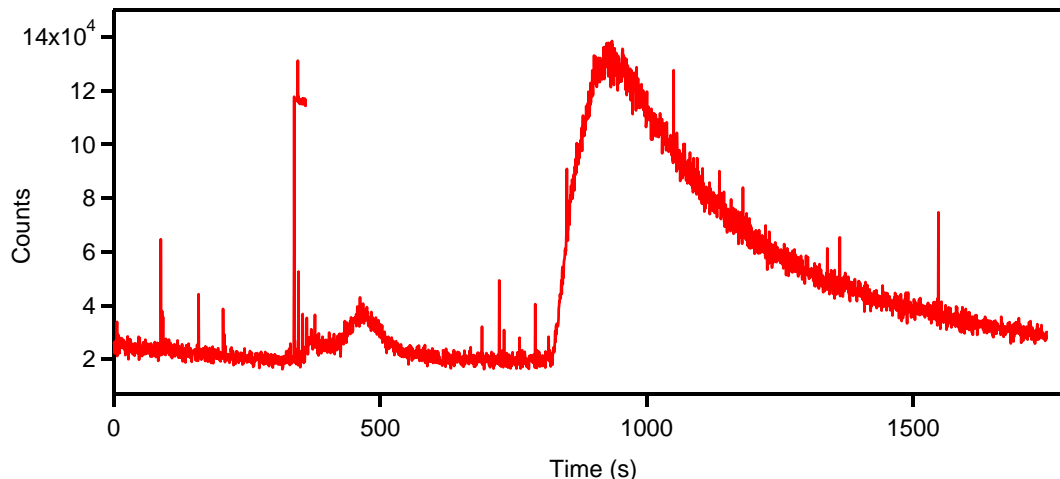


Figure S1. Chromatogram of $60 \mu\text{g L}^{-1}$ AgNp (average diameter 5 nm) and $400 \mu\text{g L}^{-1}$ dissolved Ag^+ measured by SEC-ICP-MS. The AgNps elute approximately at a time similar to other Np elution times, but the Ag^+ cations elute across a broad time range and form a poorly defined chromatographic peak. We attribute this peak shape to Ag^+ not forming complexes with EDTA, in contrast to Cd^{2+} , Zn^{2+} , and Au^{3+} which did form complexes. Only a small portion of Ag^+ is expected to complex with EDTA at the eluent pH, and the remaining Ag^+ likely interacts to the negatively-charged column media and resists elution. The run time had to be extended to 30 minutes to elute most of the dissolved Ag^+ peak. Randomly occurring spikes in signal could be caused by stray AgNp elution, and this feature was observed in multiple runs. The SEC column and eluent used in our study is not suitable for Ag analysis.

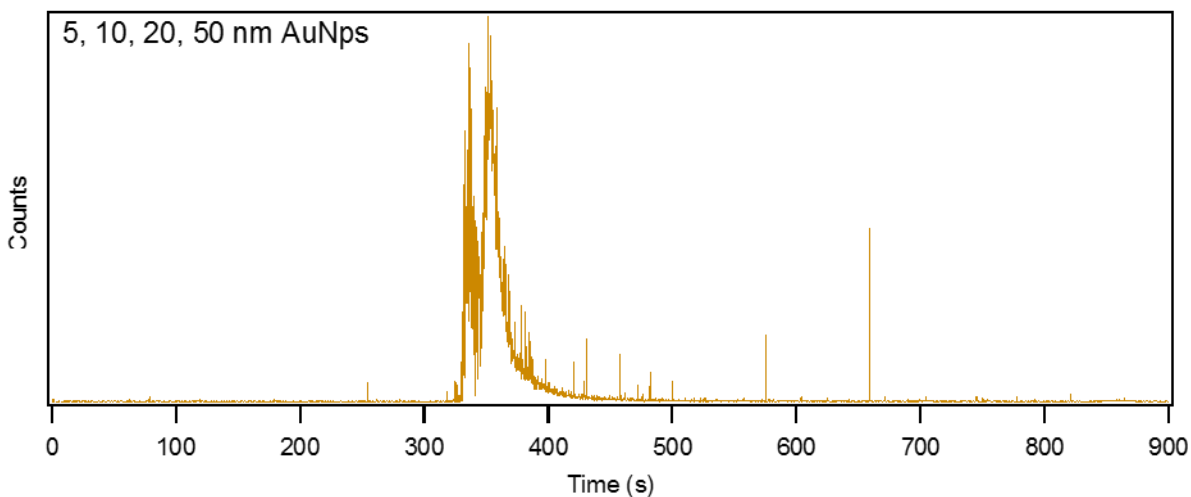


Figure S2. Chromatogram of of an aqueous suspension containing a mixture of approximately equal mass concentrations ($1 \mu\text{g L}^{-1}$) 5, 10, 20, and 50 nm sized AuNps obtained using SEC-ICP-MS. Elution of the 50 nm sized AuNps is observed first, followed by simultaneous elution of the smaller AuNps. Overall poor separation of different sized AuNPs occurs under this eluent and column condition.

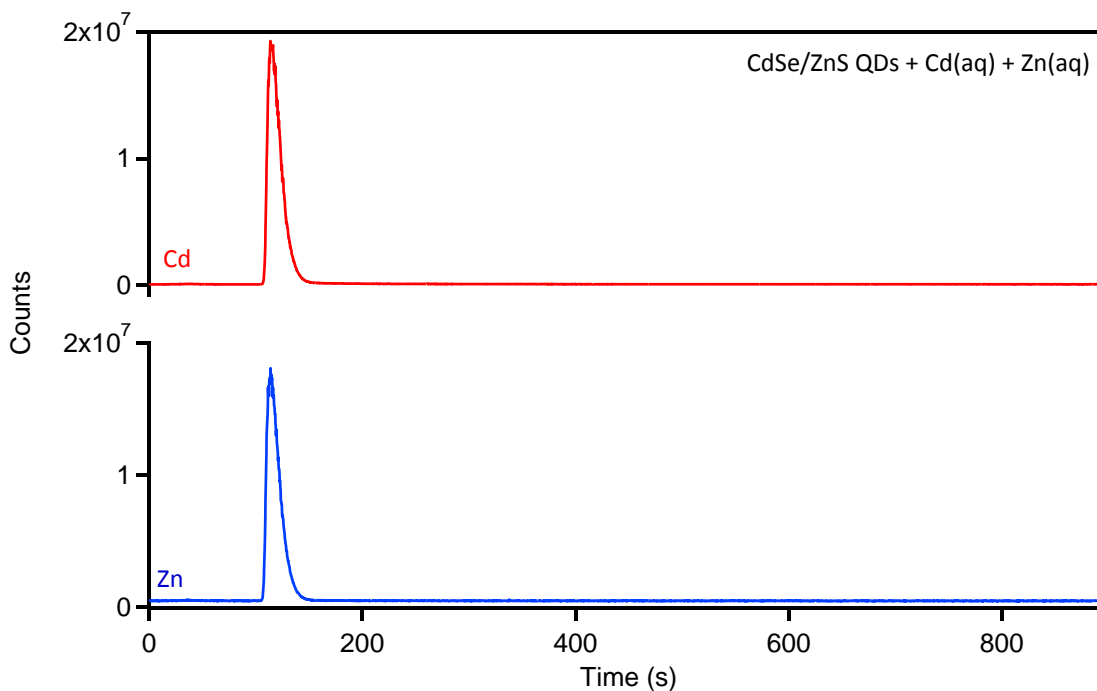


Figure S3. Chromatogram of of an aqueous suspension containing both $1000 \mu\text{g L}^{-1}$ CdSe/ZnS QDs and $400 \mu\text{g L}^{-1}$ Cd^{2+} and Zn^{2+} obtained using a C18 column attached to the HPLC followed by detection by ICP-MS. The same SEC eluent was used for this column. No separation of the QD and dissolved phases are observed. Elution of the dissolved cations occurs almost immediately due to little retention within the column, and the QDs are assumed to co-elute with the dissolved cations or to continuously elute throughout the run time, as suggested by the spikes in Cd signal over 900 s. C18 columns with this eluent therefore provide no chromatographic separation of the two phases, even though pore size (10 nm) is similar to pore size of our SEC column (12.5 nm).

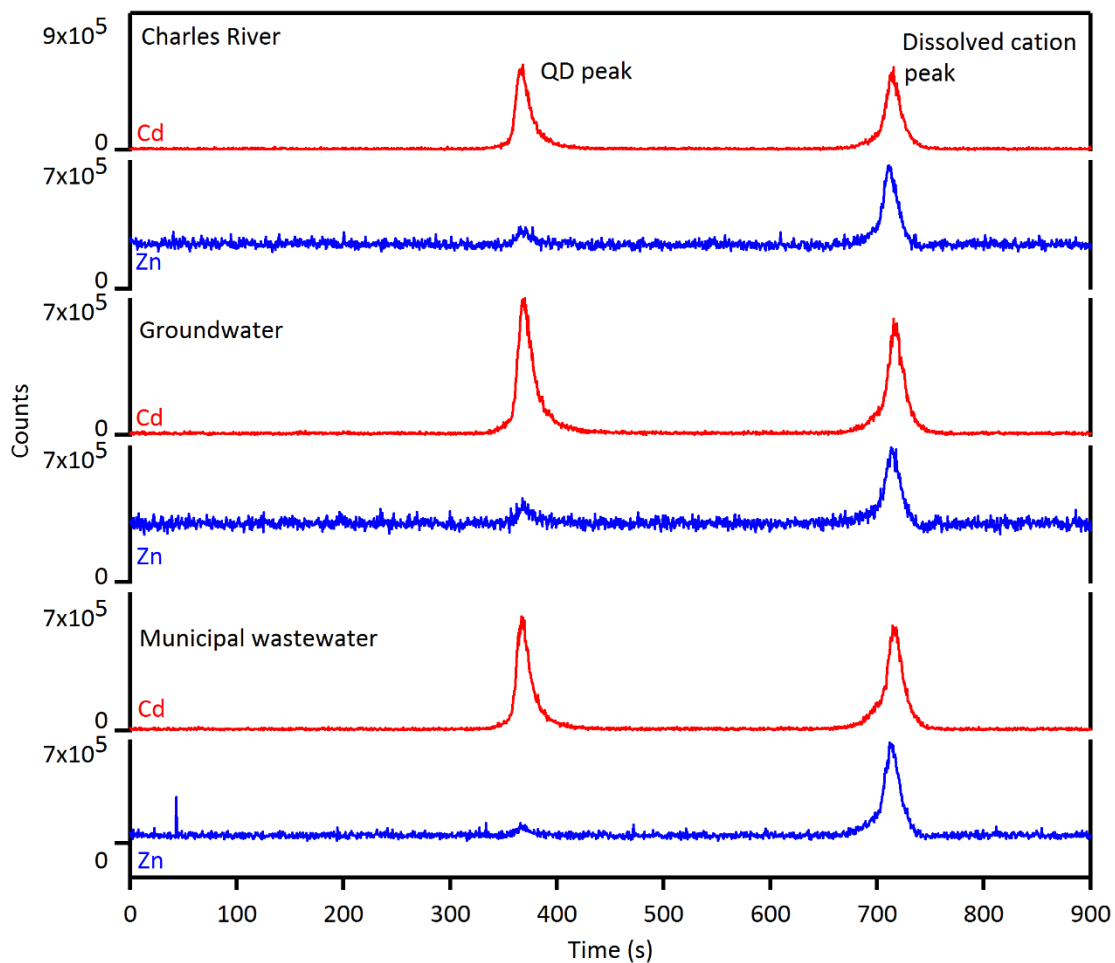


Figure 4. SEC-ICP-MS chromatograms of CdSe/ZnS QDs ($\sim 30 \mu\text{g L}^{-1}$ as QDs) and dissolved metal cations ($10 \mu\text{g L}^{-1}$) that were added into samples of municipal wastewater, Charles River water, and ground water. Measured water quality parameters are presented in Table 2.

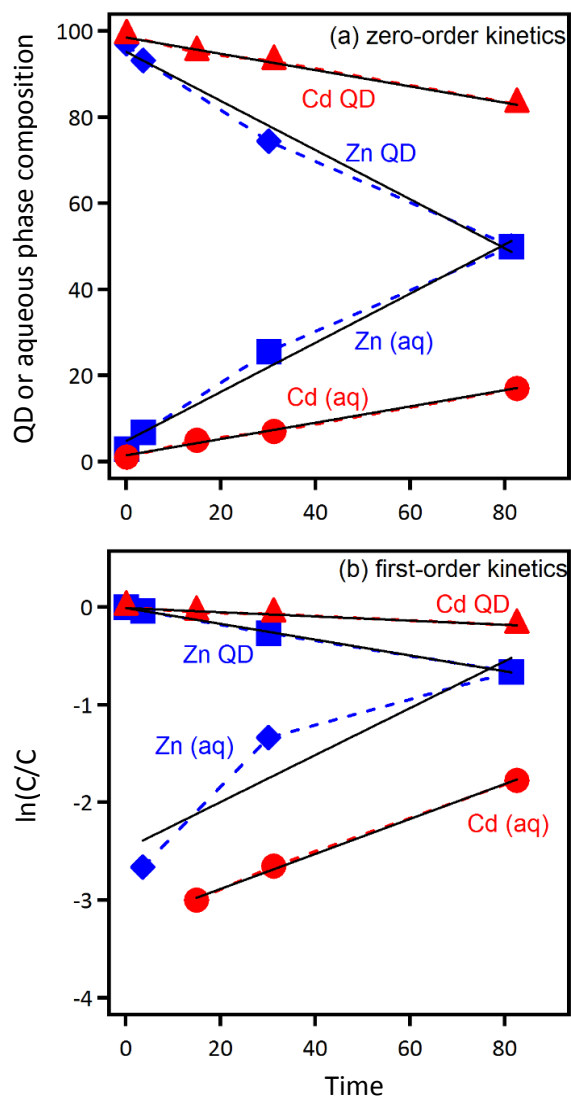


Figure S5. Kinetic model fits to measured data. (a) zero-order kinetic model, and (b) first-order kinetic model. Each model fits the data generally well. All correlation coefficients R^2 are 0.98, except for $Zn_{(aq)}$ data for first-order, which is 0.90. The equations for the regression lines are as follows:

(a) zero-order kinetics

Cd QD: $y = -0.195x + 98.8$

Zn QD: $y = -0.571x + 95.2$

Zn (aq): $y = 0.582x + 4.10$

Cd (aq): $y = 0.195x + 1.18$

(b) first-order kinetics

Cd QD: $y = -0.002x - 0.01$

Zn QD: $y = -0.008x - 0.01$

Zn (aq): $y = 0.027x - 2.65$

Cd (aq): $y = 0.02x - 3.24$