

## **Supplementary materials**

### **A. Methods**

#### **A1. X-ray photoelectron spectroscopy**

The power of CeO<sub>2</sub> NPs was deposited on a double-side tape. The base and operating chamber pressure were set at 10<sup>-7</sup> Pa. The samples were irradiated by a monochromatic Al K $\alpha$  source ( $\lambda = 8.34$  Å). The spectra were obtained with an electron take-off angle of 90°. The charge neutralizer filament was used to reduce sample charging. Survey spectra were collected using an elliptical spot with major and minor axis lengths of 2 and 1 mm, respectively, and 160 eV pass energy with a step of 0.33 eV. CasaXPS software (VAMAS) was used to analyze the cerium oxide composition. All spectra were internally calibrated to the C 1s emission (284.8 eV). The Ce3d peak was deconvoluted using CasaXPS software with doublet area ratio constrained 3:2 and doublet separation fixed at 18.1 eV. The integrated area under the curve of each deconvoluted peak was used to calculate the concentration of Ce<sup>3+</sup> and Ce<sup>4+</sup>.

#### **A2. Dissolution**

Polypropylene beakers (250 mL) were soaked in 1% HNO<sub>3</sub> overnight and rinsed with ddH<sub>2</sub>O to remove trace metal. Slide-A-Lyzer dialysis cassettes (~1 nm; 2000 molecular weight cut-off; Pierce) were injected with 1 mL of either NP suspensions at concentration of 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O or Rio Negro Amazon water. Cassettes injected with ddH<sub>2</sub>O or Rio Negro Amazon water without NPs were used as controls. The cassettes were placed in beakers containing 300 mL ddH<sub>2</sub>O on stir plates with constant slow rotation for 30 min then cassettes were transferred to new beaker with fresh ddH<sub>2</sub>O for 96 h to determine the concentration of free metal ions in test

NP suspensions. The beakers were covered with tinfoil to avoid light exposure, and reduce evaporation and production of reactive oxygen species. Water samples were collected in duplicate from each beaker at 0, 0.5, 12, 24, 36, 48, 72 and 96 h. The metal ion concentrations were measured by inductively coupled plasma mass spectroscopy (ICP-MS; Perkin Elmer, Elan 6000).

### **A3. Concentration and composition of NOM**

A Shimadzu TOC –L CPH/CPN analyzer (Shimadzu Corporation Kyoto, Japan) was used to determine dissolved organic carbon concentrations. Standards were prepared from potassium hydrogen phthalate (Mandel Scientific, Guelph, ON) at 5, 10 and 15 mg of C/L. All the samples were filtered and acidified by adding a few drops of concentrated HCl to convert dissolved inorganic carbon into volatile CO<sub>2</sub>, and then ddH<sub>2</sub>O rinses were made after every sample. Fluorescence excitation-emission matrices (FEEM) was used to determine molecular and structural composition of the samples. A Varian Cary Eclipse Fluorescence spectrophotometer (Varian, Mississauga, ON, Canada) scanned the emission of wavelengths at 250 to 600 nm in 1 nm increments for intervals of 10 nm excitation wavelengths between 200 and 450 nm to create FEEM plots. The photomultiplier tube was at high detection (800V) and the scan speed was set at 400 nm minute<sup>-1</sup>.

### **A4. Inductively Coupled Plasma-Mass Spectroscopy**

Water samples from the exposure experiments and dialysis were treated with 12 µL per 10 mL of 15.7 M trace metal nitric acid right after the collections. Analysis for cerium (<sup>140</sup>Ce) was performed using an Agilent 8800 Triple Quadrupole ICP-MS (ICP-MS/MS) with RF power of

1550 W and a RF reflected power of 18 W. The ICP-MS/MS was operated with a microMist nebulizer and nickel/copper cones. An inline internal standard system was employed with a solution of 0.5 ppm to correct for instrumental drift. Samples passed through dialysis tubing were analyzed using standards covering a range of 0.0002 ppm to 10 ppm. For particle samples two sets of standards were prepared: 1) from diluting purchased 1,000 Ce standard stock solution (Alfa Aesar), 2) through suspending 300 ppm of CeO<sub>2</sub> particles in 18 MΩ water to cover a range of 0.4-9 ppm of particles. To reduce particle aggregation and sample heterogeneity, samples containing particles samples were sonicated for 1 minute before analysis and throughout the sample uptake using a Fisher 505 Sonic Dismembrator.

#### **A5. Hematoxylin and eosin staining**

The fixed gills were rinsed and immersed in 50% ethanol for 4 hours and then processed by Leica tp1020 tissue processor (Leica Biosystems) for 12 hours. After the 12 hour period, gills were embedded in paraffin wax. Tissue blocks were cut at 5μm in the orientation of lamellar sagittal section by microtome (Leica Biosystems). Tissue slides were processed for histology examination following the standard techniques with hematoxylin and eosin staining. Briefly, slides were immersed with toluene for 5 minutes twice and then 100% ethanol for 2 minutes twice. After that, slides were immersed in 90%, 70%, 50% and distilled water for 2 minutes once and then rinsed with cold distilled water for 15 minutes. After rinsing, slides were immersed in 70% ethanol for 2 minutes once, eosin for 30 second once, and 100% ethanol for 2 minutes twice and toluene for 2 minutes twice. Slides were kept in toluene until they were coverslipped with DPX. Slides were kept in 37 °C oven overnight for the DPC to solidify.

## B. Tables and figures

**Table S1.** The concentrations (mg L<sup>-1</sup>) of dissolved organic carbon (mg L<sup>-1</sup>) in stock NOM water and NOM water without NPs at 48 hours and 96 hours with and without UV exposure. Values are mean  $\pm$  standard deviation. Groups share the same letter indicates no significance ( $p > 0.05$ ).

Samples	UV exposure	Dissolved organic carbon (mg L <sup>-1</sup> )
Stock NOM	No	14.78 $\pm$ 1.10 <sup>a</sup>
NOM at 0 mg L <sup>-1</sup> , 48 hours	Yes	14.07 $\pm$ 0.69 <sup>a</sup>
NOM at 0 mg L <sup>-1</sup> , 48 hours	No	13.01 $\pm$ 0.50 <sup>a</sup>
NOM at 0 mg L <sup>-1</sup> , 96 hours	Yes	13.50 $\pm$ 0.56 <sup>a</sup>
NOM at 0 mg L <sup>-1</sup> , 96 hours	No	14.09 $\pm$ 0.56 <sup>a</sup>

**Table S2.** Absolute Fractions (arb units) of humic acid, fulvic acid, tyrosine and tryptophan-like fraction of experimental DOC's under Ultraviolet (UV) light and no UV light means are  $\pm$  S.E.M (n=3 per treatment). Groups share the same letter indicates no significance ( $p > 0.05$ ).

Sample	Humic Acid	Fulvic Acid	Tyrosine	Tryptophan
Stock	2.9 $\pm$ 0.04 <sup>a</sup>	1.2 $\pm$ 0.002 <sup>a</sup>	0.11 $\pm$ 0.01 <sup>a</sup>	0.15 $\pm$ 0.01 <sup>a</sup>
48 hour No UV	2.9 $\pm$ 0.05 <sup>a</sup>	1.30 $\pm$ 0.01 <sup>b</sup>	0.1 $\pm$ 0.02 <sup>a</sup>	0.15 $\pm$ 0.02 <sup>a</sup>
48 hour UV	2.5 $\pm$ 0.05 <sup>b</sup>	1.60 $\pm$ 0.007 <sup>c</sup>	0.18 $\pm$ 0.006 <sup>bd</sup>	0.12 $\pm$ 0.03 <sup>a</sup>
96 hour No UV	3.0 $\pm$ 0.02 <sup>a</sup>	1.4 $\pm$ 0.01 <sup>d</sup>	0.13 $\pm$ 0.004 <sup>ad</sup>	0.20 $\pm$ 0.007 <sup>a</sup>
96 hour UV	2.3 $\pm$ 0.0004 <sup>c</sup>	1.85 $\pm$ 0.0007 <sup>e</sup>	0.21 $\pm$ 0.007 <sup>bc</sup>	0.19 $\pm$ 0.008 <sup>a</sup>

**Table S3.** The ICP-MS analysis of total cerium concentrations from the water samples collected during exposure of CeO<sub>2</sub> NPs at 0, 12, 48 and 96 hours. The results of nominal concentration of 0.5 mg L<sup>-1</sup> were not shown in the table because they were all below detection limit (BDL, 0.048 mg L<sup>-1</sup>).

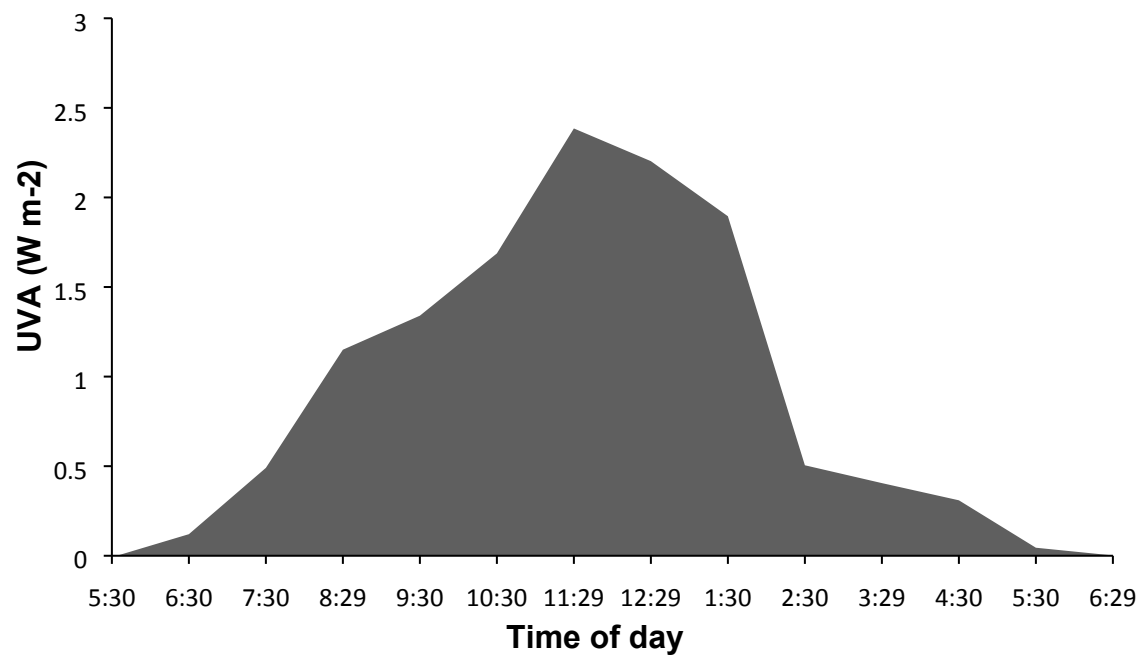
Nominal Concentration (mg L <sup>-1</sup> )	Time (hours)	Water	UV	Detected concentration (mg L <sup>-1</sup> )
2	0	ddH <sub>2</sub> O	No	0.73
2	12	ddH <sub>2</sub> O	No	0.060
2	48	ddH <sub>2</sub> O	No	BDL
2	96	ddH <sub>2</sub> O	No	BDL
2	0	ddH <sub>2</sub> O	Yes	0.56
2	12	ddH <sub>2</sub> O	Yes	0.098
2	48	ddH <sub>2</sub> O	Yes	0.28
2	96	ddH <sub>2</sub> O	Yes	0.80
2	0	NOM	No	0.83
2	12	NOM	No	0.45
2	48	NOM	No	0.32
2	96	NOM	No	0.19
2	0	NOM	Yes	0.83
2	12	NOM	Yes	0.50
2	48	NOM	Yes	0.46
2	96	NOM	Yes	0.52
5	0	ddH <sub>2</sub> O	No	2.2
5	12	ddH <sub>2</sub> O	No	1.6
5	48	ddH <sub>2</sub> O	No	0.98
5	96	ddH <sub>2</sub> O	No	0.88
5	0	ddH <sub>2</sub> O	Yes	1.8
5	12	ddH <sub>2</sub> O	Yes	1.3
5	48	ddH <sub>2</sub> O	Yes	1.2
5	96	ddH <sub>2</sub> O	Yes	1.2
5	0	NOM	No	1.9
5	12	NOM	No	0.30
5	48	NOM	No	0.19
5	96	NOM	No	0.028
5	0	NOM	Yes	1.7
5	12	NOM	Yes	0.36
5	48	NOM	Yes	0.16
5	96	NOM	Yes	0.35

**Table S4.** The polydispersity index (PDI), PDI width (nm) and hydrodynamic diameter (HDD) of CeO<sub>2</sub> NPs at nominal concentration of 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) measured by DLS at 0, 2, 4, 6, 12, 24, 48, 72 and 96 hours.

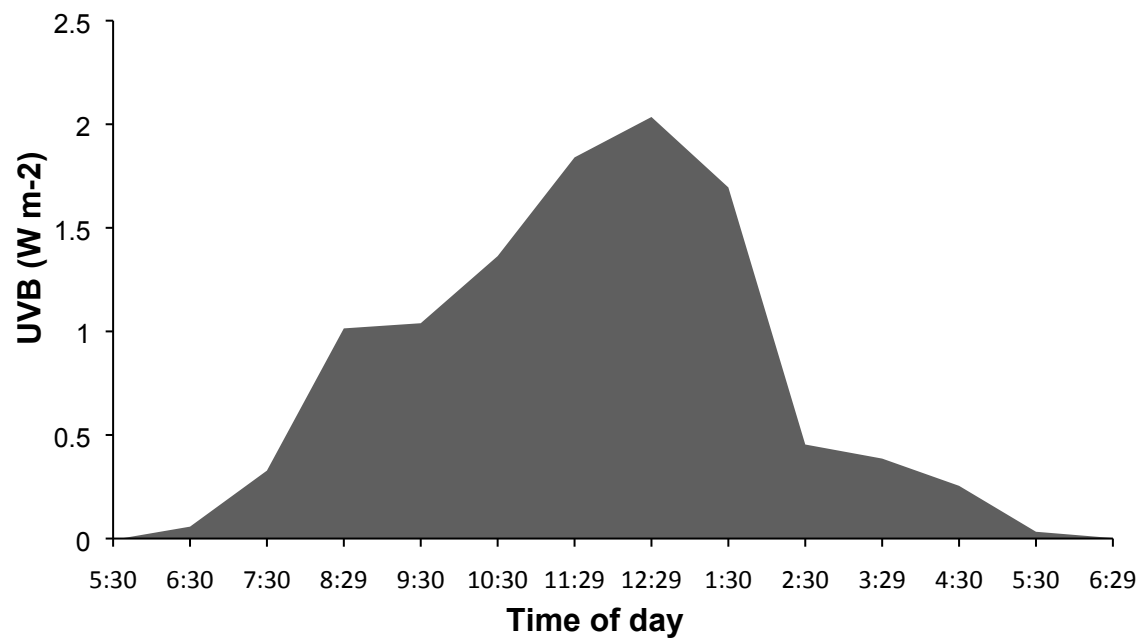
Time (hours)	Nominal concentration (mg/L)	Average PDI	Average PDI width (nm)	Average HDD (nm)	SEM PDI	SEM PDI width (nm)	SEM HDD (nm)
0	0.5	0.957	2965.7	2994.3	0.043	905.5	877.5
	2	1.000	3782.7	3783.3	0.000	1025.2	1025.7
	5	1.000	3120.0	3120.3	0.000	769.0	768.8
2	0.5	1.000	1991.0	1991.3	0.000	91.3	91.3
	2	0.964	2002.0	2025.0	0.036	615.3	600.3
	5	1.000	1738.0	1738.0	0.000	87.6	87.6
4	0.5	0.933	1795.7	1827.1	0.067	458.6	427.6
	2	0.967	2048.0	2074.7	0.033	327.5	306.4
	5	0.924	1572.7	1615.3	0.076	346.5	306.5
6	0.5	0.876	1189.9	1224.7	0.062	203.4	182.4
	2	0.893	1542.8	1603.1	0.074	434.9	400.1
	5	0.932	1323.3	1390.7	0.025	116.1	135.3
12	0.5	0.861	1166.8	1248.6	0.070	201.0	181.3
	2	0.799	819.2	908.1	0.088	133.8	98.1
	5	0.730	607.2	707.8	0.057	99.7	96.5
24	0.5	0.753	812.2	904.7	0.118	259.5	236.4
	2	0.592	501.1	646.8	0.056	73.2	64.4
	5	0.576	399.8	522.8	0.112	76.7	49.8
48	0.5	0.635	572.3	717.0	0.026	39.0	34.1
	2	0.561	392.9	516.4	0.097	90.9	73.8
	5	0.462	290.8	426.5	0.034	32.0	36.6
72	0.5	0.614	523.9	596.6	0.062	37.4	48.0
	2	0.639	540.9	676.7	0.046	40.4	36.7
	5	0.447	284.2	409.9	0.072	87.4	103.7
96	0.5	0.614	497.2	633.5	0.060	46.7	33.7
	2	0.612	527.1	665.9	0.073	101.9	87.1
	5	0.447	273.7	406.3	0.051	44.3	47.1

**Table S5.** The polydispersity index (PDI), PDI width (nm) and hydrodynamic diameter (HDD) of CeO<sub>2</sub> NPs at nominal concentration of 0.5, 2 and 5 mg L<sup>-1</sup> in Rio Negro water (NOM+) measured by DLS at 0, 2, 4, 6, 12, 24, 48, 72 and 96 hours.

Time (hours)	Nominal concentration (mg/L)	Average PDI	Average PDI width (nm)	Average HDD (nm)	SEM PDI	SEM PDI width (nm)	SEM HDD (nm)
0	0.5	0.688	674.9	797.5	0.087	178.9	161.6
	2	0.966	1742.6	1760.5	0.034	427.4	409.8
	5	0.997	1787.3	1789.0	0.003	293.3	291.9
2	0.5	0.673	574.2	713.9	0.069	95.2	75.9
	2	0.871	886.2	942.6	0.096	161.2	139.0
	5	0.831	673.3	733.3	0.085	122.2	104.6
4	0.5	0.627	500.3	622.2	0.104	104.3	88.6
	2	0.832	813.8	887.6	0.069	104.1	76.3
	5	0.838	728.5	793.6	0.034	150.3	155.9
6	0.5	0.707	546.8	646.0	0.116	98.6	82.2
	2	0.816	792.0	854.6	0.120	275.2	242.7
	5	0.695	508.0	601.8	0.038	98.5	102.4
12	0.5	0.645	574.3	514.3	0.058	62.3	54.8
	2	0.693	647.8	647.8	0.063	28.3	28.3
	5	0.753	718.4	718.4	0.128	120.1	120.1
24	0.5	0.583	473.7	473.7	0.083	15.3	15.3
	2	0.583	444.9	444.9	0.032	44.9	44.9
	5	0.488	346.1	346.1	0.044	22.2	22.2
48	0.5	0.347	302.4	302.4	0.014	20.8	20.8
	2	0.400	357.7	357.7	0.049	54.8	54.8
	5	0.363	317.4	317.4	0.044	27.5	27.5
72	0.5	0.452	355.9	355.9	0.052	60.6	60.6
	2	0.412	275.2	275.6	0.040	30.6	30.2
	5	0.367	229.5	229.5	0.024	19.3	19.3
96	0.5	0.420	193.6	303.7	0.055	19.3	40.6
	2	0.492	199.3	285.2	0.110	31.8	12.6
	5	0.440	142.1	214.2	0.053	12.9	6.8

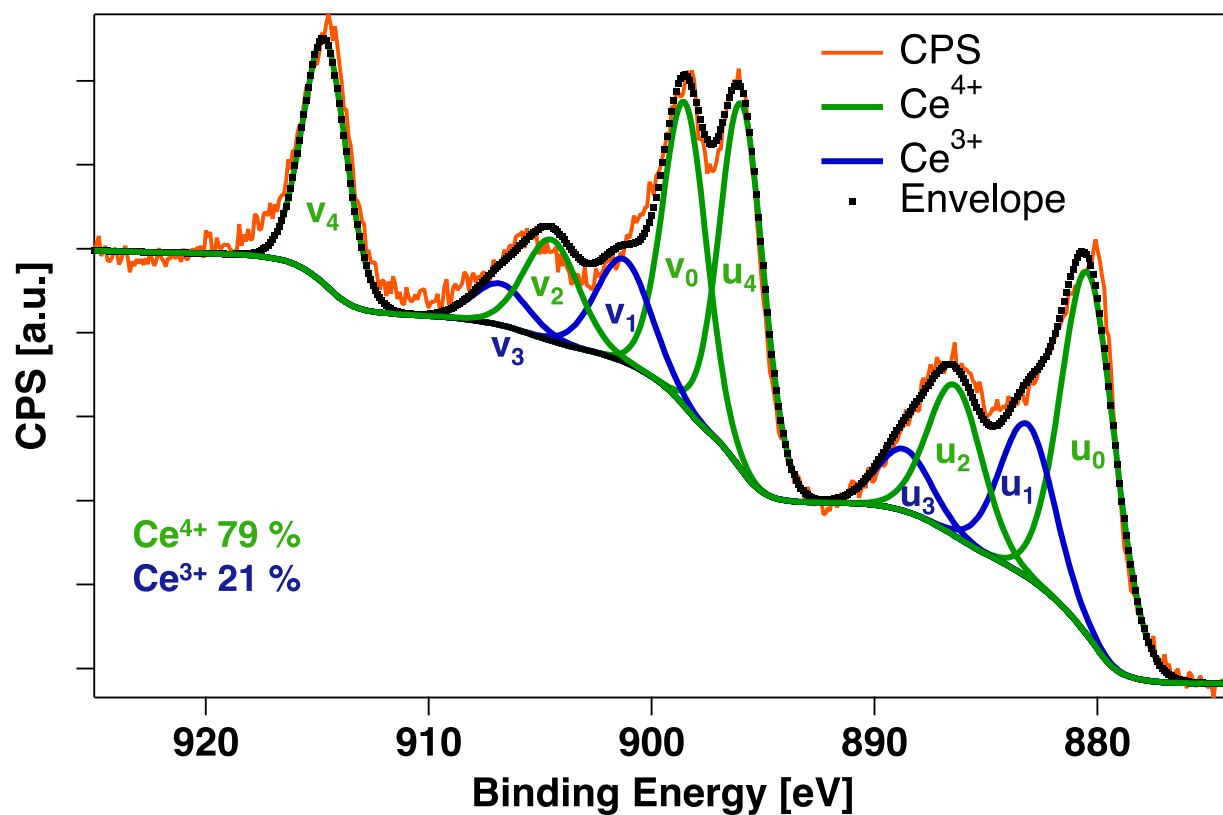


**Figure S1.** The average of UVA (W m<sup>-2</sup>) in Rio Negro water (Brazil) from 5:30 to 18:30.

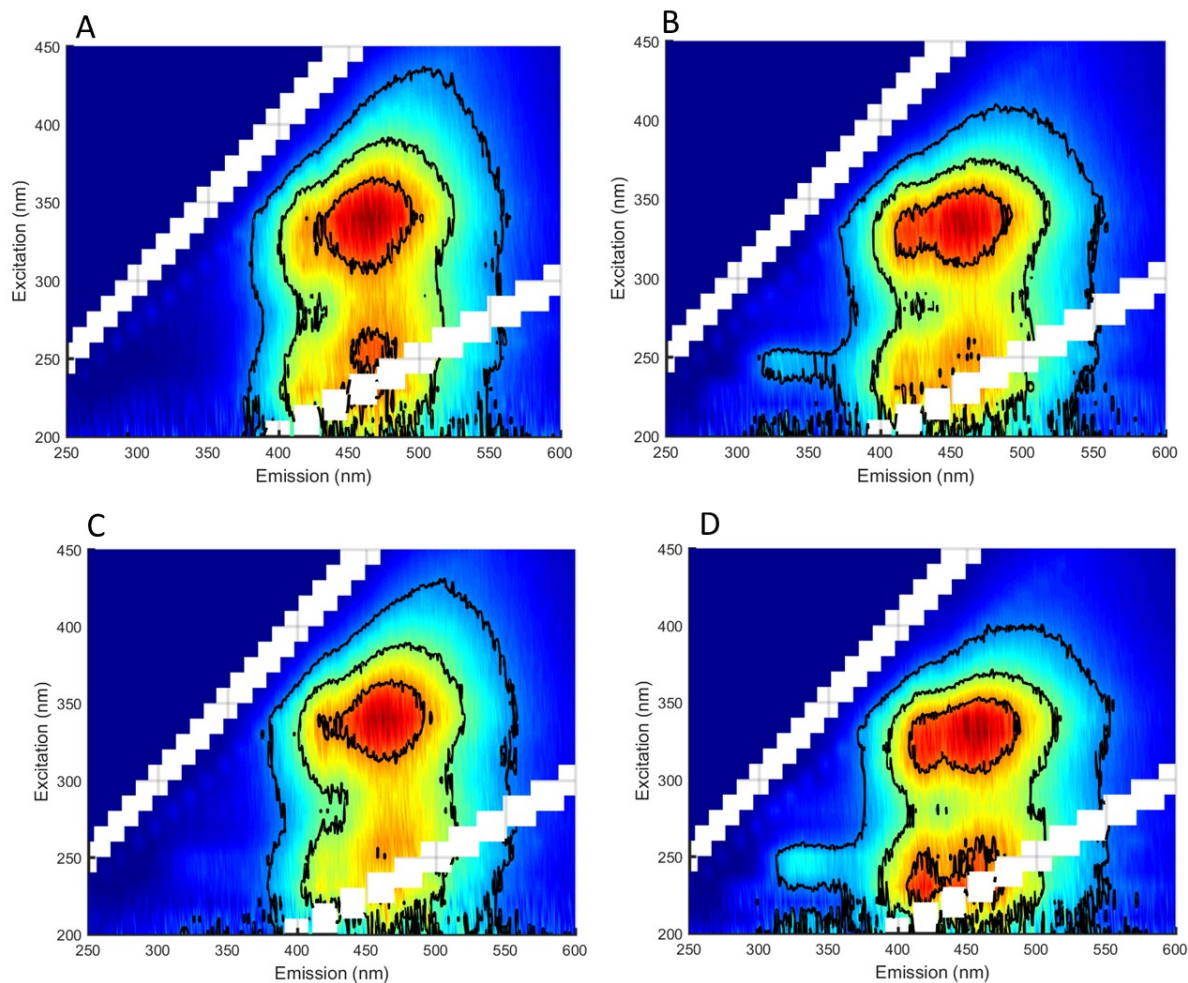


**Figure S2.** The average of UVB (W m<sup>-2</sup>) in Rio Negro water (Brazil) from 5:30 to 18:30.

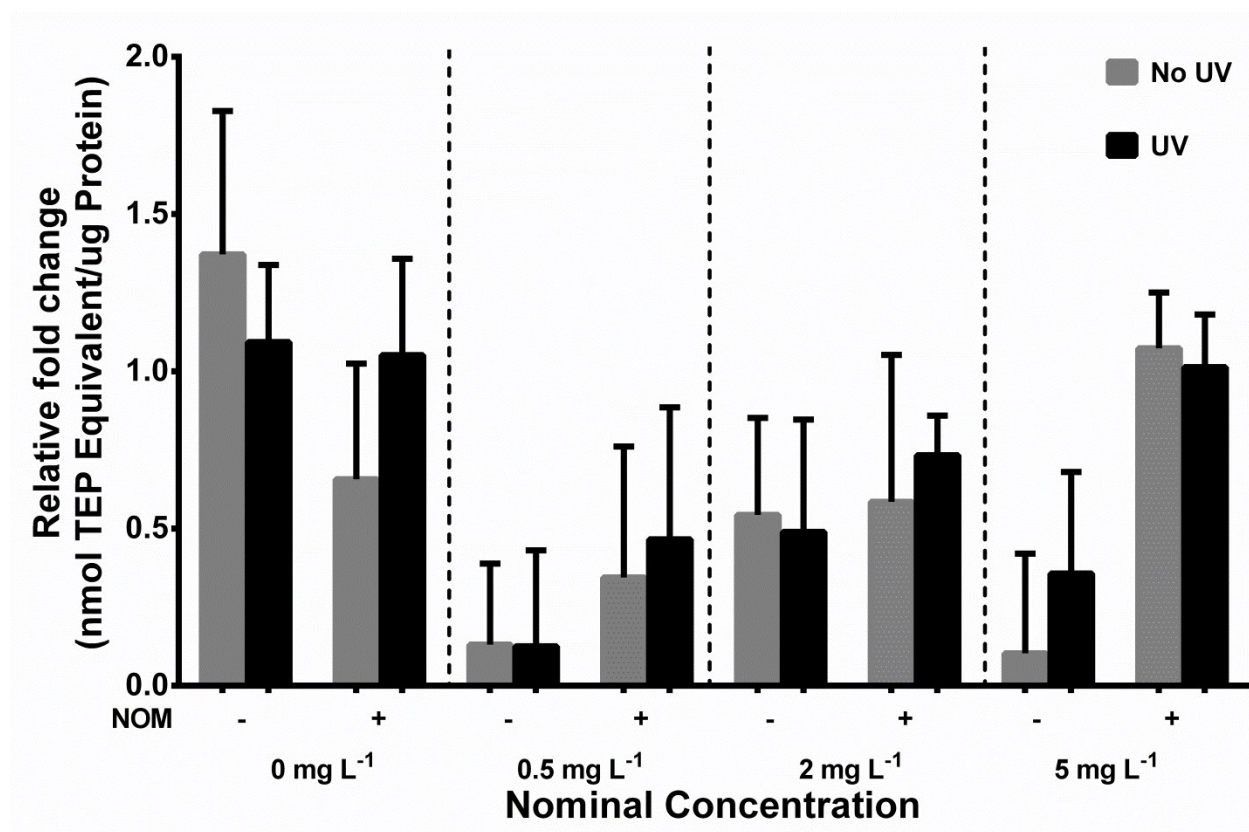




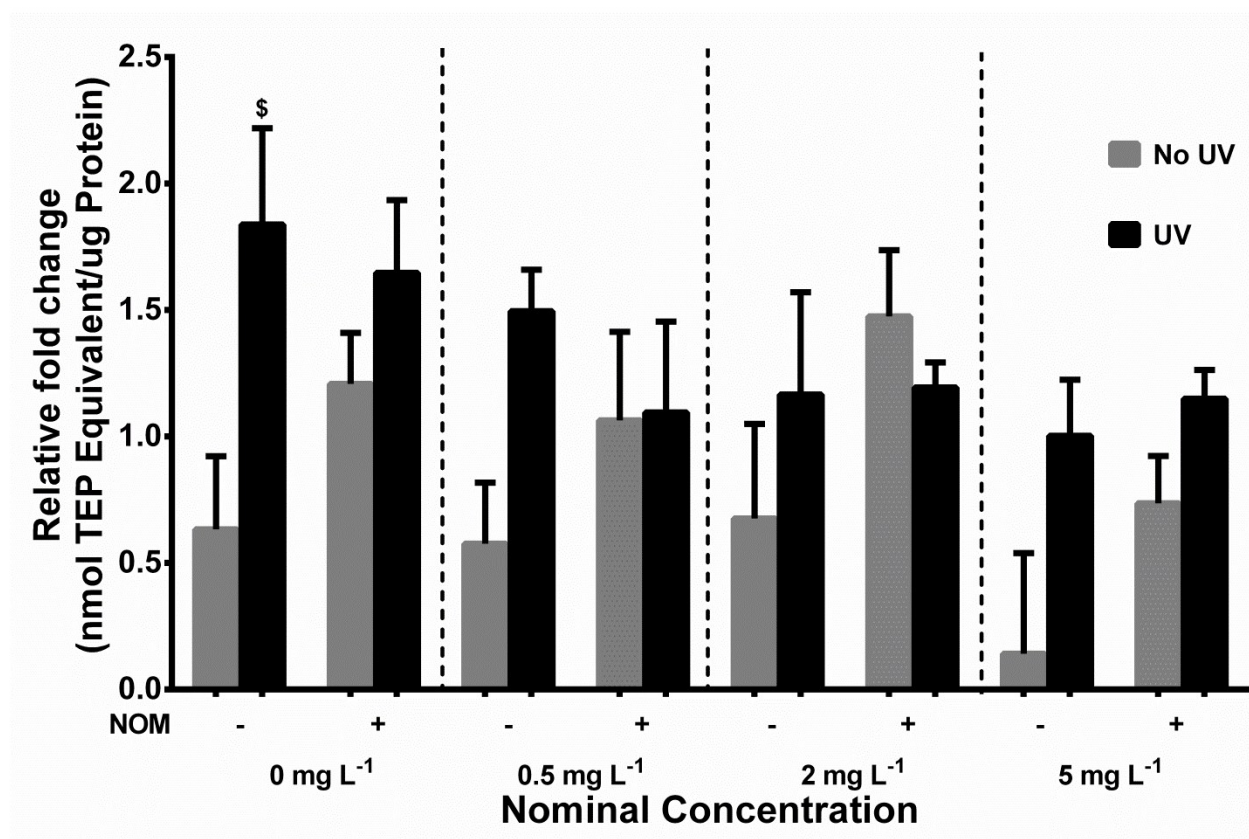
**Figure S3.** Narrow scan Ce 3d XPS spectrum of CeO<sub>2</sub> NPs samples. Three final states of Ce<sup>4+</sup> are expressed as u<sub>0</sub> (v<sub>0</sub>), u<sub>2</sub> (v<sub>2</sub>) and u<sub>4</sub> (v<sub>4</sub>), for Ce3d<sub>3/2</sub> (Ce3d<sub>5/2</sub>). Two final states of Ce<sup>3+</sup> are expressed as u<sub>1</sub> (v<sub>1</sub>) and u<sub>3</sub> (v<sub>3</sub>), for Ce3d<sub>3/2</sub> (Ce3d<sub>5/2</sub>).



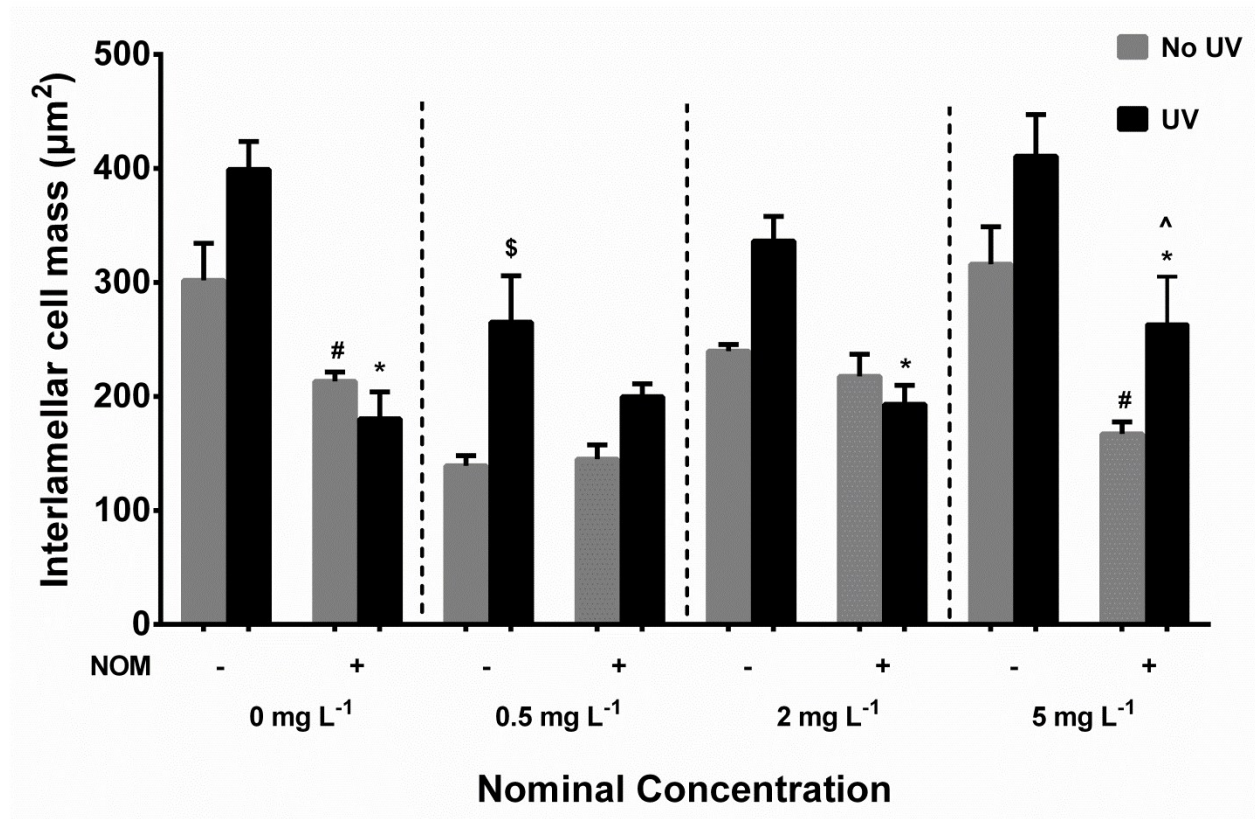
**Figure S4.** Fluorescence excitation-emission matrices (FEEM) where A) NOM no UV 48 hours; B) NOM UV 48 hours; C) NOM no UV 96 hours and D) NOM UV.



**Figure S5.** Lipid peroxidation in gills of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 96 hours (N=6). Relative fold change (NOM without UV at 0 mg L<sup>-1</sup> were used as reference) of TBARS expressed as nmol TEP Equivalent/ $\mu$ g protein.

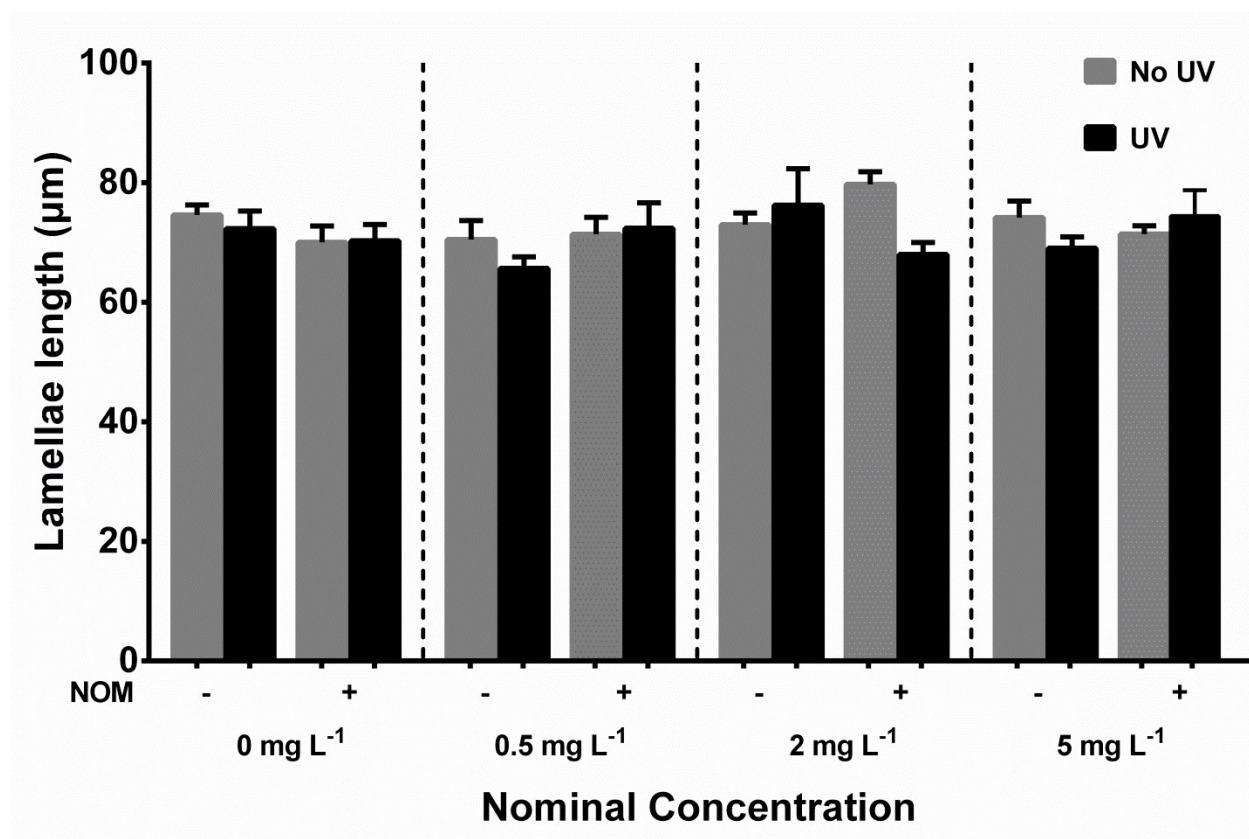


**Figure S6.** Lipid peroxidation in livers of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 96 hours (N=6). Relative fold change (NOM without UV at 0 mg L<sup>-1</sup> were used as reference) of TBARS expressed as nmol TEP Equivalent/μg protein. Values are mean ± SEM.

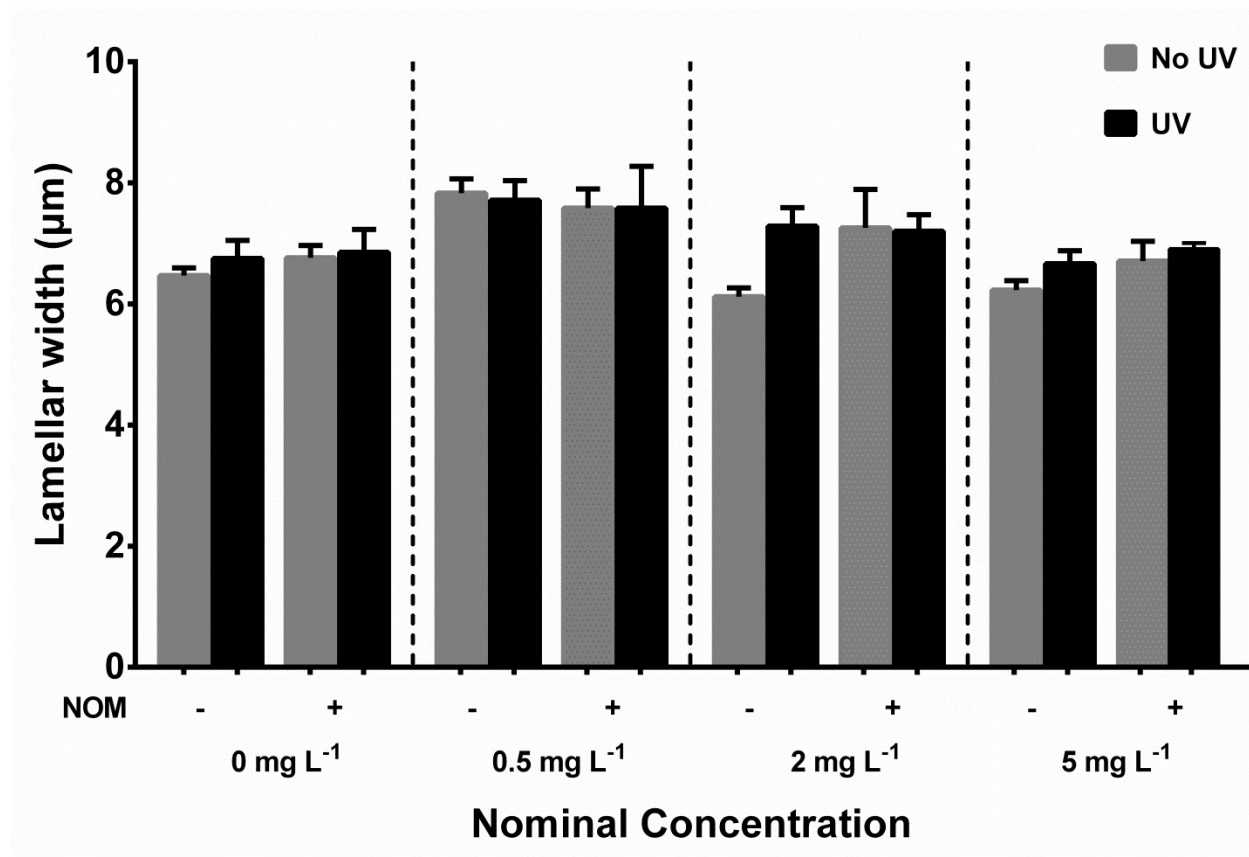


**Figure S7.** The interlamellar cell mass (µm<sup>2</sup>) of gills of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 96 hours (N=4). Values are mean ± SEM. \* indicates NOM significantly reduces ILCM under UV light. # indicates NOM significantly reduces ILCM without UV light. \$ indicates UV light significantly increases ILCM in ddH<sub>2</sub>O.

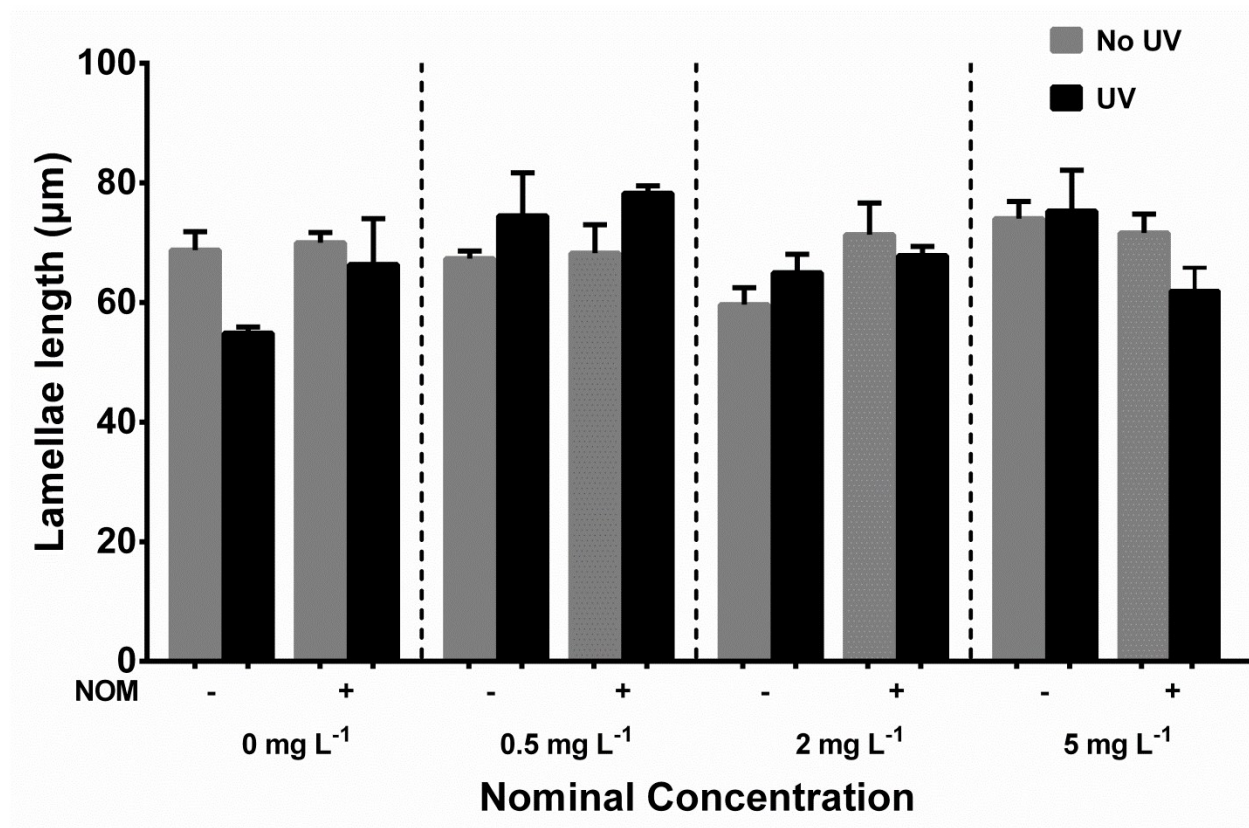




**Figure S8.** The lamellar length ( $\mu\text{m}$ ) of gills of cardinal tetras exposed to  $\text{CeO}_2$  NPs suspension at nominal concentrations of 0, 0.5, 2 and 5  $\text{mg L}^{-1}$  in  $\text{ddH}_2\text{O}$  (NOM-) and Rio Negro water (NOM+) with or without UV light for 48 hours ( $N=4$ ). Values are mean  $\pm$  SEM.

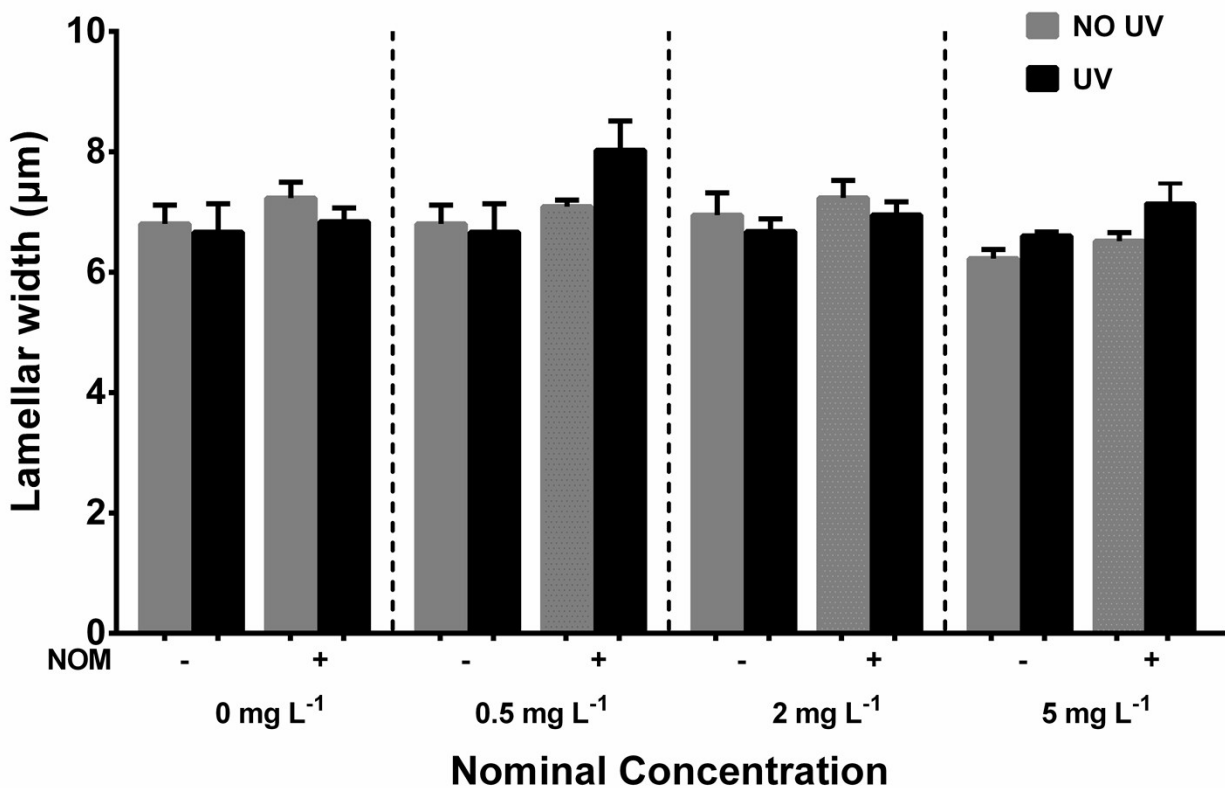


**Figure S9.** The lamellar width (μm) of gills of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 48 hours (N=4). Values are mean ± SEM.



**Figure S10.** The lamellar length (μm) of gills of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 96 hours (N=4). Values are mean ± SEM.





**Figure S11.** The lamellar length (μm) of gills of cardinal tetras exposed to CeO<sub>2</sub> NPs suspension at nominal concentrations of 0, 0.5, 2 and 5 mg L<sup>-1</sup> in ddH<sub>2</sub>O (NOM-) and Rio Negro water (NOM+) with or without UV light for 96 hours (N=4). Values are mean ± SEM.