

1 Supporting Information

2 **Stability of CeO₂ nanoparticles derived from paints and**
3 **stains: insights under controlled and environmental**
4 **scenarios**

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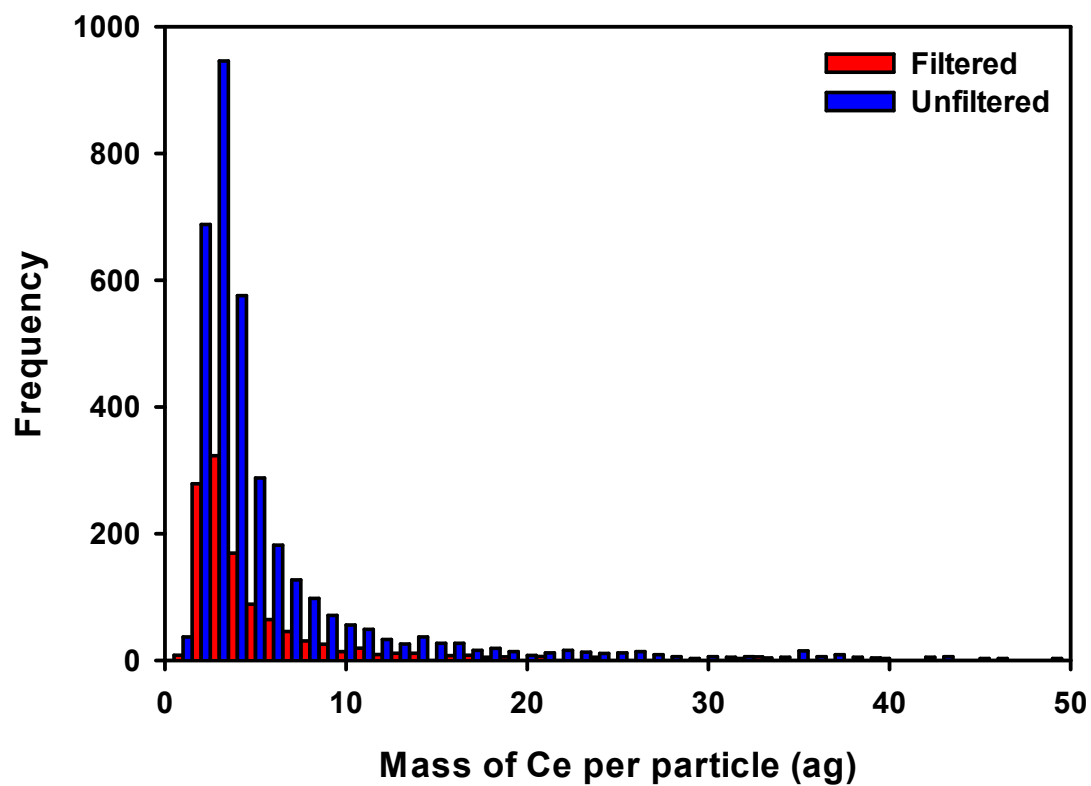
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14 **Effect of sample filtration**

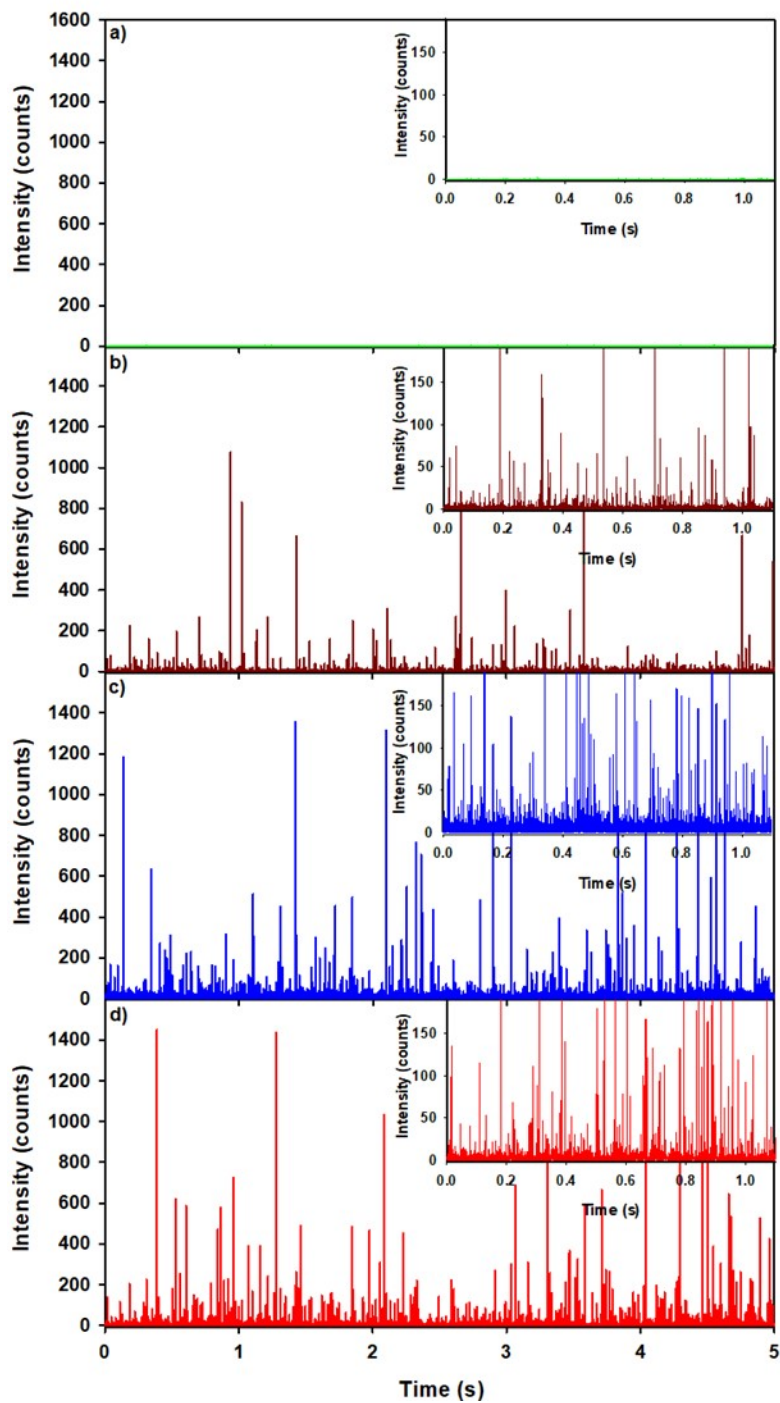
15 Although the precipitation can be analyzed, unfiltered, suspended particles and aggregates may
16 occasionally cause blockages in the ICP-MS introduction system. Given that we were mainly
17 interested in quantifying the smaller (nano) particles, the effect of 0.45 μm membrane filtration
18 was examined for a natural sample. For a precipitation sample examined before and after
19 filtration, filtration decreased background Ce concentrations by $60 \pm 7\%$, which was mainly
20 attributed to the adsorption of dissolved Ce on the filters. The decrease of dissolved Ce actually
21 led to a decrease in the size detection limit (SDL) and a small shift of the observed particle size
22 distributions (PSD) to lower sizes. However, in spite of having a lower SDL after filtration, NP
23 numbers decreased by $55 \pm 15\%$. Although this decrease was mainly attributed to the removal of
24 large particles (i.e. $>0.45 \mu\text{m}$), some losses of small Ce-containing NP were occurring to the filters
25 via adsorption (**Fig. S1**).



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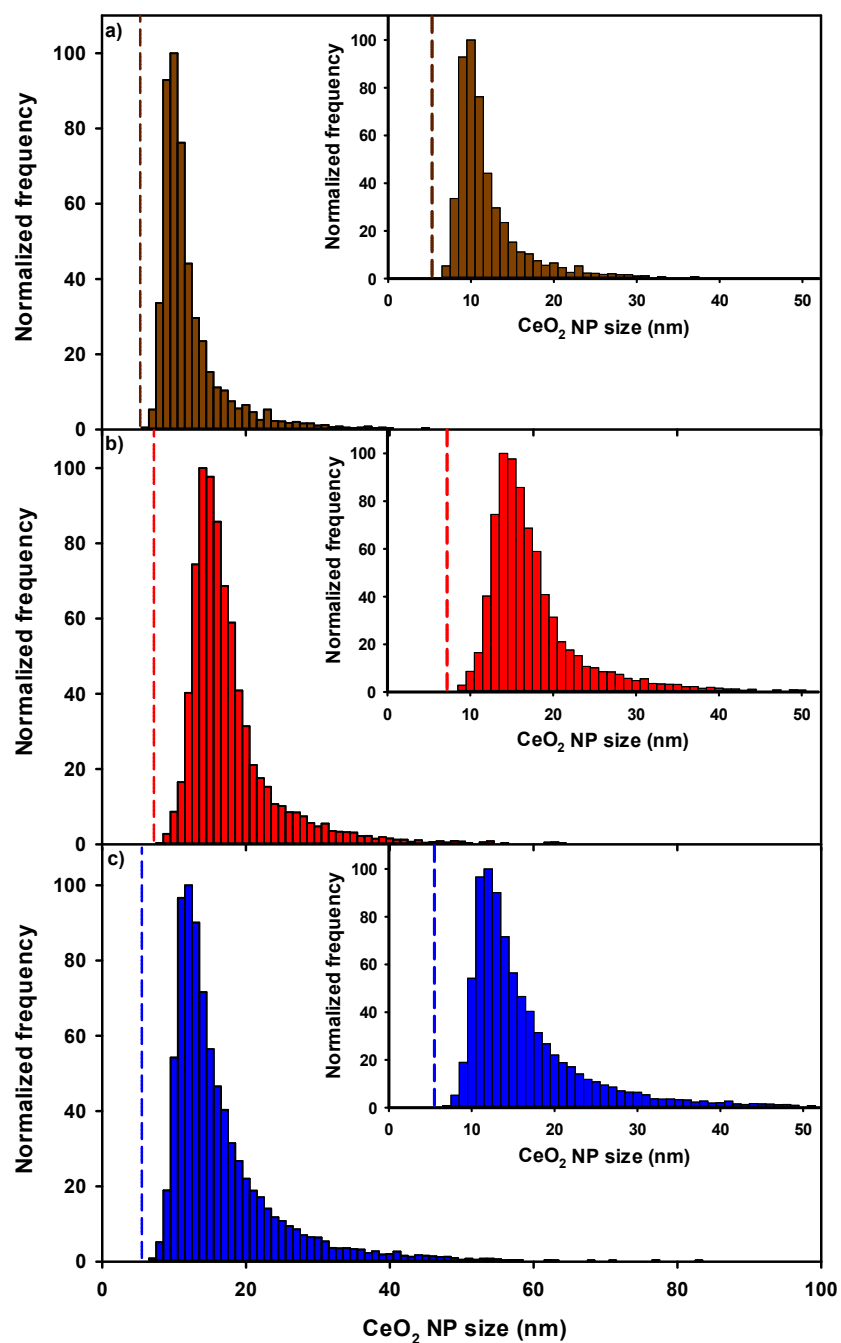
27 **Figure S1.** Mass distributions of Ce NP in a precipitation sample with or without filtration on a 0.45 μm
28 PVDF membrane. Measurements were performed using SP-ICP-MS and a dwell time of 50 μs .

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31 **Figure S2.** Time resolved signal (raw data) for ^{140}Ce in (a) Milli-Q water; (b) precipitation, (c) paint and (d)
 32 stain. Paint and stain were diluted 2500x. For better readability, only 5 s of data collection were shown,
 33 using a total acquisition time of 50 s. Measurements were obtained using SP-ICP-MS with a 50 μs dwell
 34 time.



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36 **Figure S3.** Calculated particle size distributions of Ce NP in (a) precipitation, (b) paint and (c) stain. Paint
 37 and stain were diluted 2500x. NP sizes were calculated by assuming that the particles were spherical CeO_2
 38 particles with a density of $7.13 \text{ kg} \cdot \text{dm}^{-3}$. The dashed lines correspond to the calculated size detection
 39 limits. Measurements were performed on a sector field SP-ICP-MS using a dwell time of $50 \mu\text{s}$.

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41 **Table S1.** Ratios of Ce to La in precipitation, paint, and stain, determined with SP-ICP-MS with a dwell time
 42 of 50 μ s. Paint and stain were diluted 2500x. Means and standard deviations were obtained from triplicate
 43 samples.

Sample	Ce NPs / La NPs	Dissolved Ce / Dissolved La
Precipitation	1.6 \pm 0.6	2.7 \pm 0.7
Paint	26.7 \pm 0.1	2.0 \pm 0.3
Stain	80.5 \pm 11.1	3.2 \pm 0.4

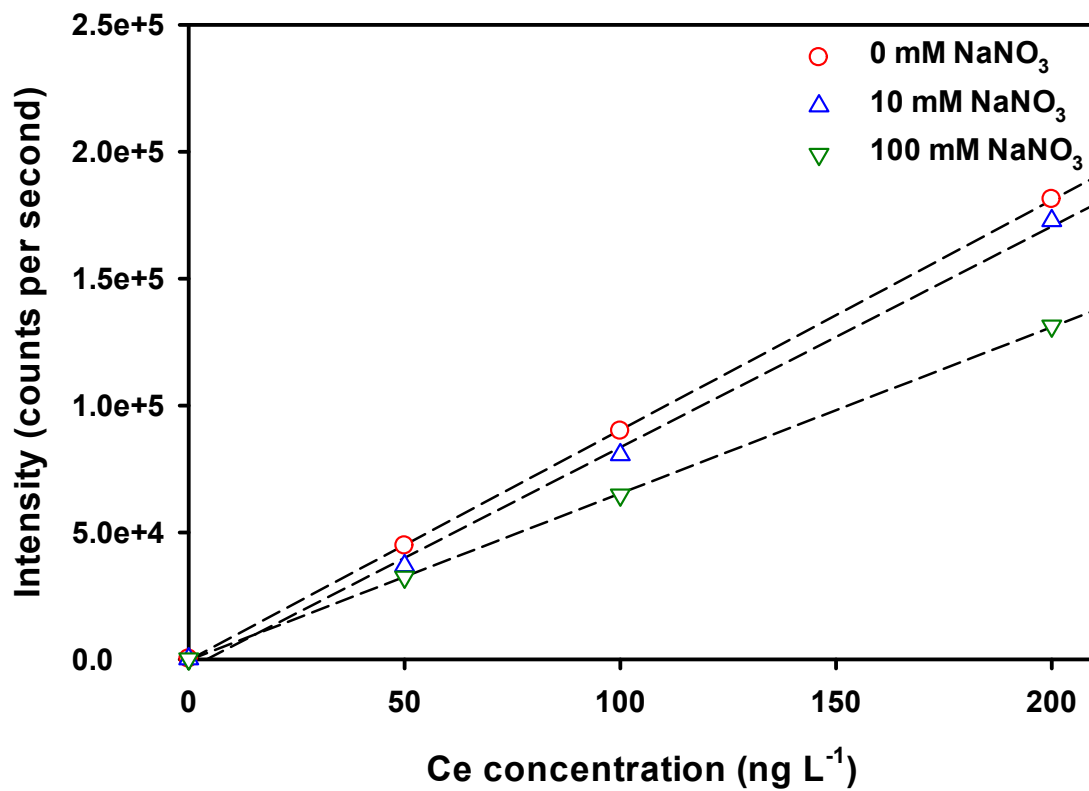
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45 **Table S2.** Size detection limits for Ce in the blanks and samples analyzed with SP-ICP-MS with a dwell time
 46 of 50 μ s. Paint and stain were diluted 2500x.

	Size detection limit (nm)	
	Milli-Q water	4.9
	Milli-Q water + 10 mM NaNO ₃	4.9
	Milli-Q water + 100 mM NaNO ₃	6.1
Blank	Milli-Q water + 2 mg L ⁻¹ NOM	4.9
	Milli-Q water + 10 mg L ⁻¹ NOM	4.9
	Acetate buffer (pH = 4.0)	4.9
	Bicarbonate buffer (pH = 7.0)	4.9
	Milli-Q water + CeO ₂ NP	4.9
Sample	Precipitation	5.3
	Diluted paint	7.2
	Diluted stain	5.5

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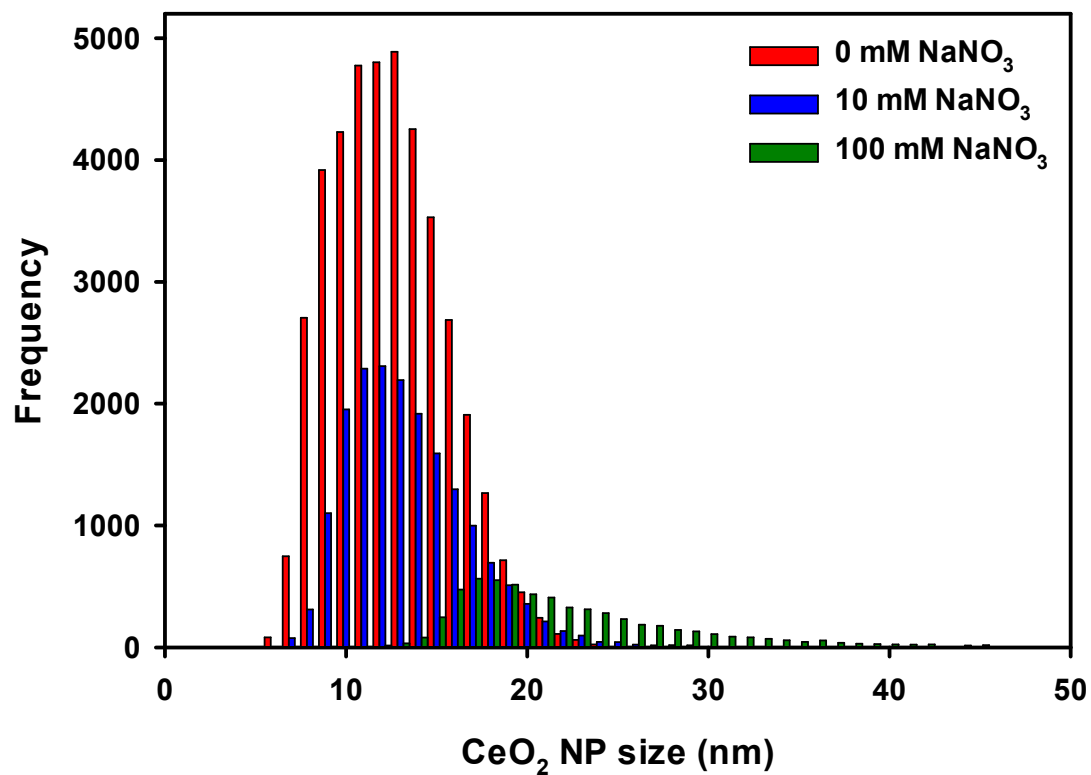
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50 **Figure S4.** Calibration curves performed using Ce standards with three different concentrations of NaNO₃.
51 The measured sensitivities were 863, 811 and 604 cps ng L⁻¹ for standards obtained in the presence of 0,
52 10 and 100 mM of NaNO₃, respectively. Measurements were performed using SP-ICP-MS and a dwell time
53 of 50 μs.

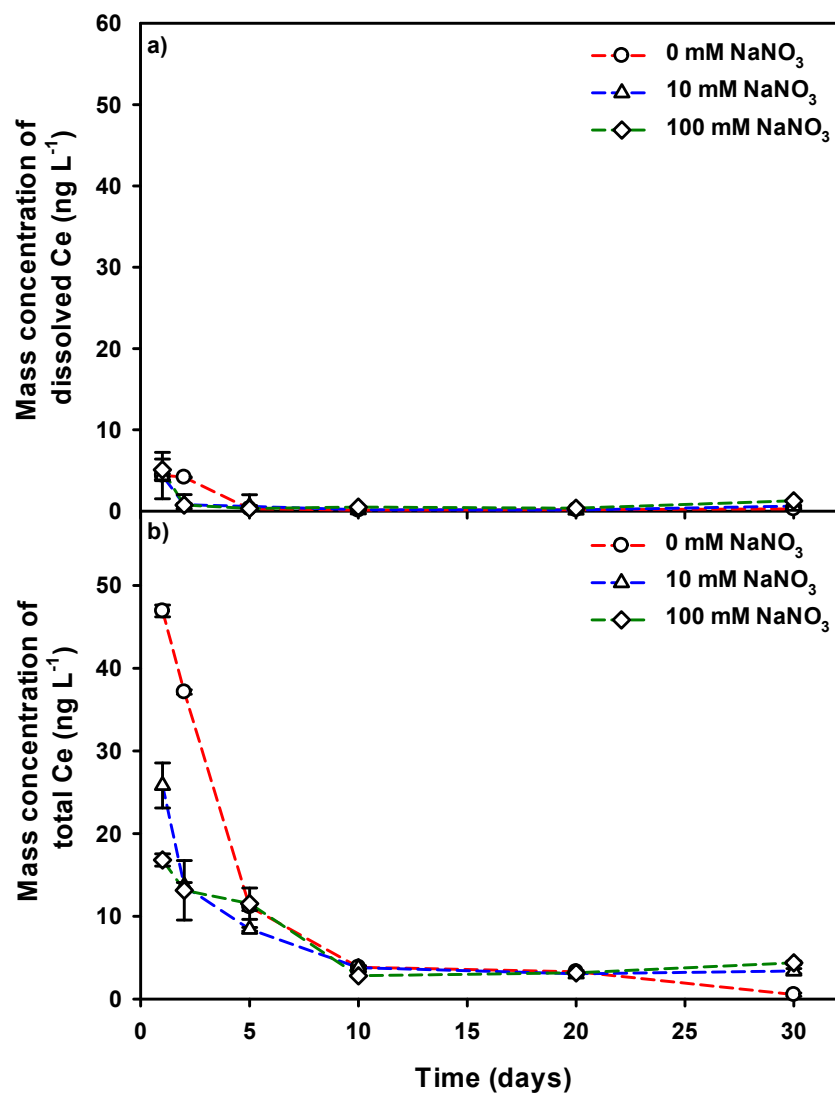
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56 **Figure S5.** Particle size distribution of CeO₂ NP in a suspension of engineered CeO₂ NP spiked into Milli-Q
 57 water with three different ionic strengths. Measurements were performed using SP-ICP-MS and a dwell
 58 time of 50 μs.

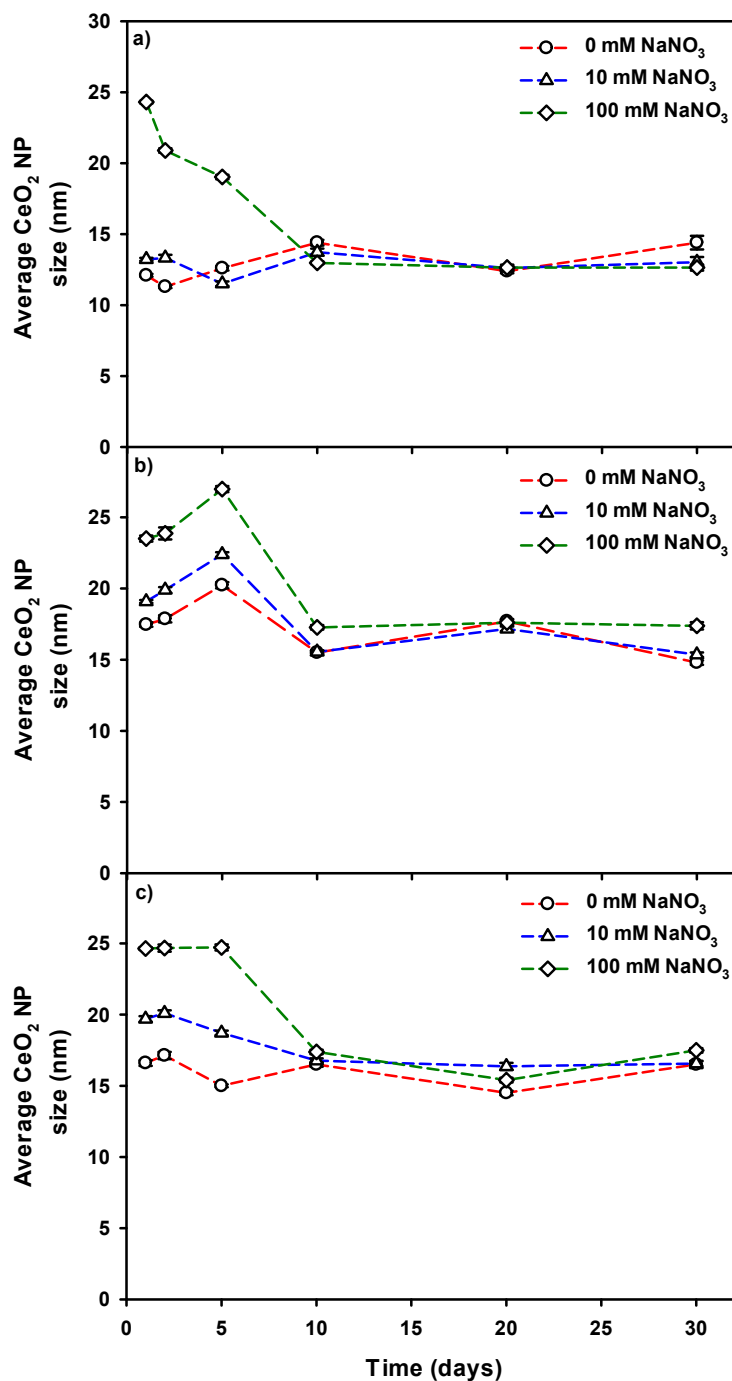
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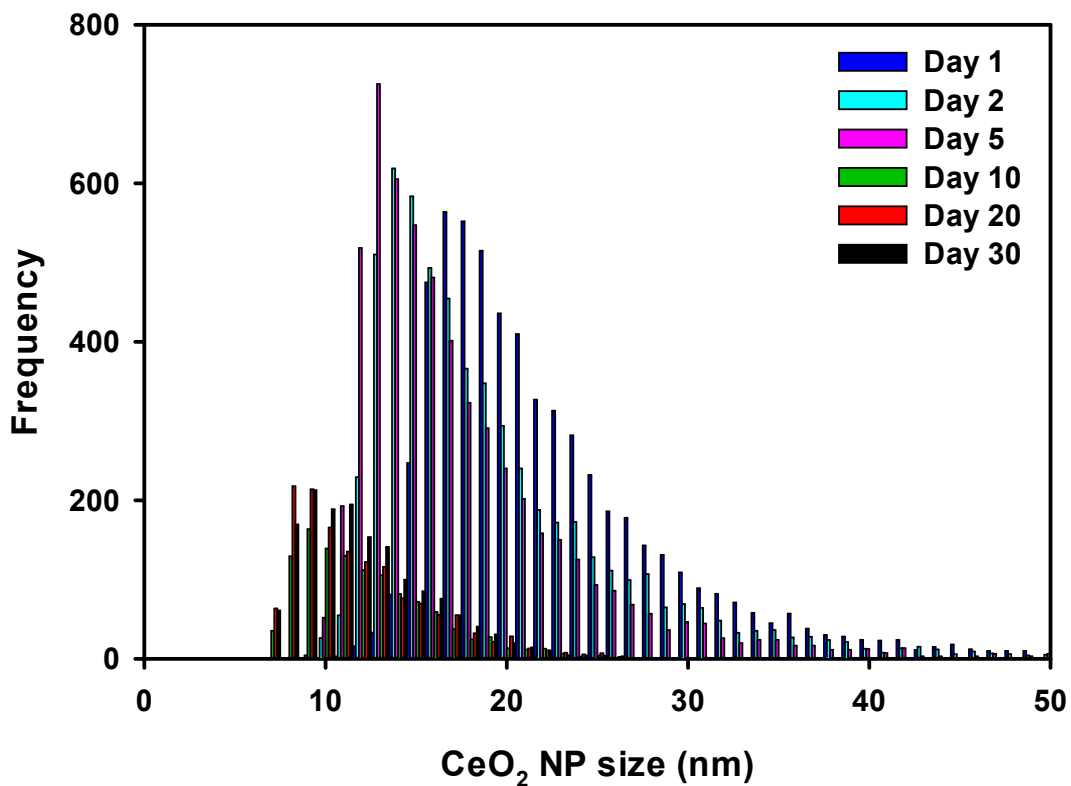
61 **Figure S6.** Mass concentrations of **(a)** dissolved and **(b)** total Ce in a suspension of engineered CeO₂ NP,
 62 spiked into Milli-Q water at three different ionic strengths, as a function of time. Error bars correspond to
 63 standard deviations obtained from triplicate analysis. Measurements were performed using SP-ICP-MS
 64 and a dwell time of 50 μs.

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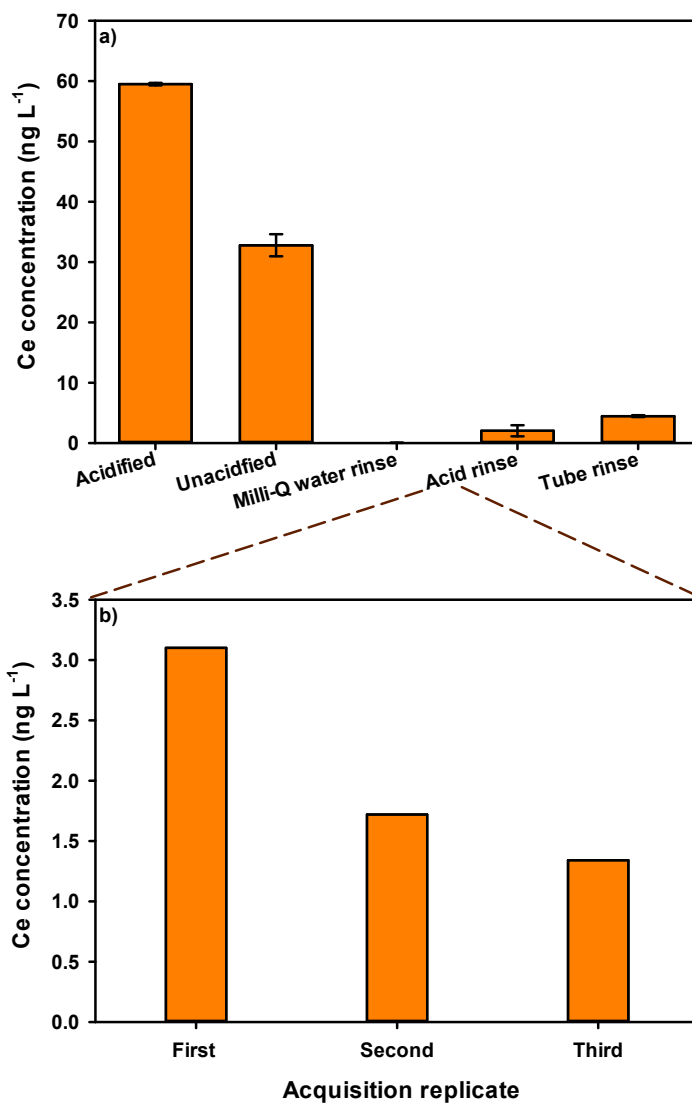
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67 **Figure S7.** Average CeO₂ NP sizes in **(a)** a suspension of engineered CeO₂ NP, **(b)** paint and **(c)** stain spiked
 68 into Milli-Q water with three different ionic strengths, as a function of time. Paint and stain were diluted
 69 2500x. SDL ranged from **(a)** 4.8 to 5.1 nm, **(b)** 7.0 to 7.2 nm, and **(c)** 5.4 to 5.5 nm. NP sizes were calculated
 70 by assuming that the particles were spherical CeO₂ particles with a density of 7.13 kg. dm⁻³. Error bars
 71 correspond to standard deviations obtained from triplicate analysis. Measurements were performed
 72 using SP-ICP-MS and a dwell time of 50 μs.



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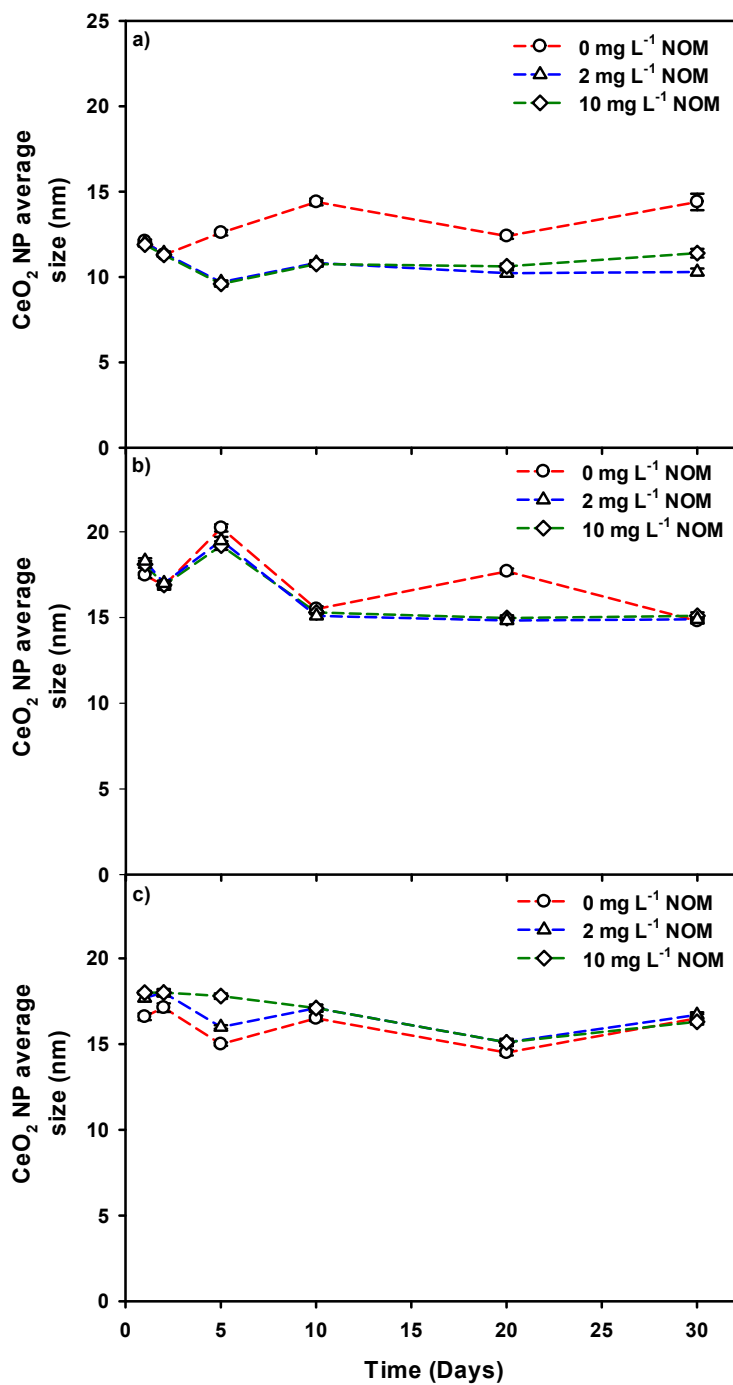
74 **Figure S8.** Particle size distributions of CeO₂ NP in a suspension of engineered CeO₂ NP spiked into Milli-Q
 75 water with 100 mM of NaNO₃. SDL ranged from 6.1 nm (Day 1) to 6.0 nm (Day 30). Measurements were
 76 performed using SP-ICP-MS and a dwell time of 50 μs.



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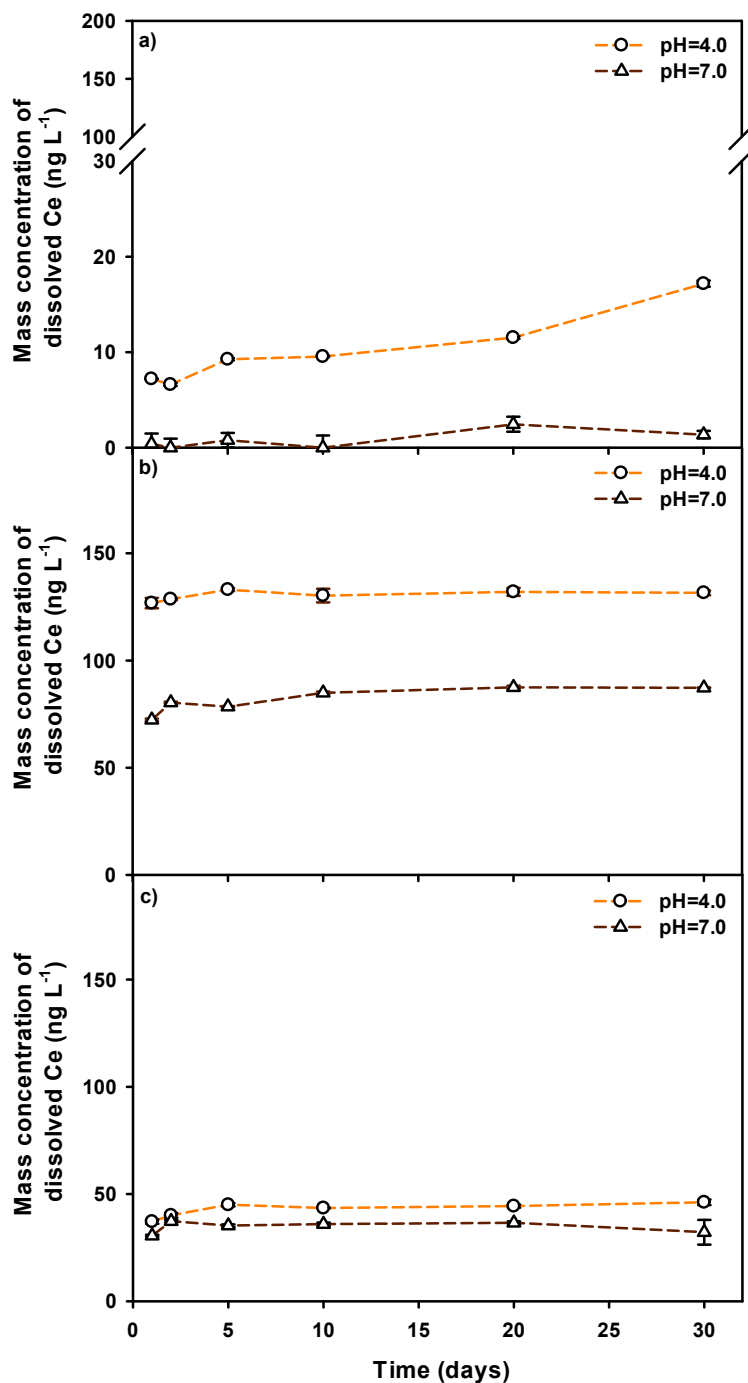
78 **Figure S9. (a)** Concentration of dissolved Ce measured in a solution of almost 60 ng L⁻¹ ionic Ce prepared
 79 in Milli-Q water without acidification. Adsorptive losses to the ICP-MS and sample tube were evaluated
 80 by measuring Ce in: (i) a Milli-Q water rinse; (ii) Successive (triplicate) rinses in 2% HNO₃ (Figure S9b) (iii)
 81 Milli-Q water rinse of the sample tube; (iv) 2% HNO₃ rinse of the sample tube. Measurements were
 82 performed using SP-ICP-MS and a dwell time of 50 μs.

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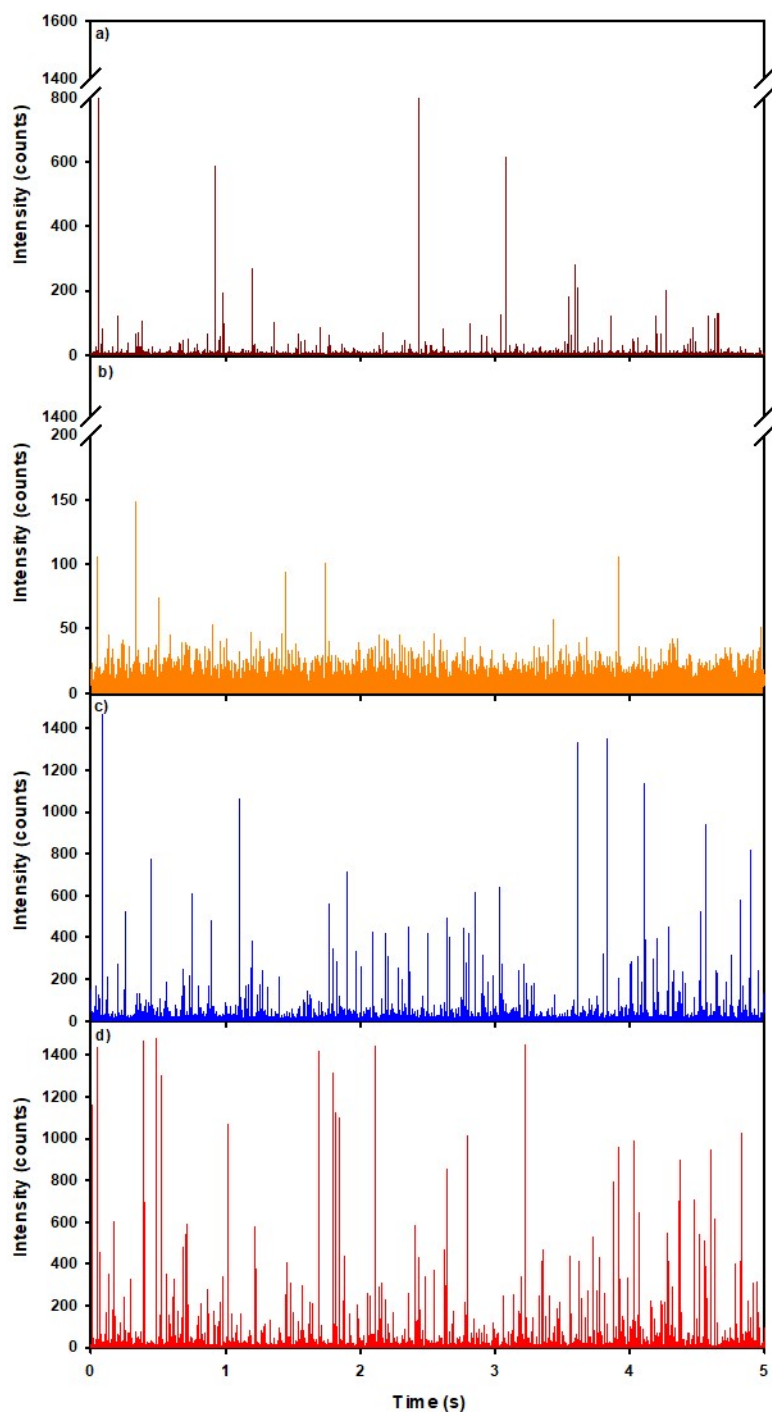
85 **Figure S10.** Average CeO₂ NP sizes in (a) a suspension of engineered CeO₂ NP, (b) paint and (c) stain spiked
 86 into Milli-Q water with three different contents of natural organic matter, as a function of time. Paint and
 87 stain were diluted 2500x. SDL ranged from (a) 4.8 to 5.1 nm, (b) 7.0 to 7.2 nm, and (c) 5.4 to 5.5 nm. NP
 88 sizes were calculated by assuming that the particles were spherical CeO₂ particles with a density of 7.13
 89 kg. dm⁻³. Error bars correspond to standard deviations obtained from triplicate analysis. Measurements
 90 were performed using SP-ICP-MS and a dwell time of 50 μs.



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92 **Figure S11.** Mass concentration of dissolved Ce in **(a)** engineered CeO₂ NP, **(b)** paint and **(c)** stain spiked
 93 into acetate buffer with pH = 4.0 or bicarbonate buffer with pH = 7.0, as a function of time. Paint and stain
 94 were diluted 2500x. SDL ranged from **(a)** 4.8 to 5.1 nm, **(b)** 7.0 to 7.2 nm, and **(c)** 5.4 to 5.5 nm. Error bars
 95 correspond to standard deviations obtained from triplicate analysis. Measurements were performed
 96 using SP-ICP-MS and a dwell time of 50 μs.

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99 **Figure S12.** Time resolved signal for ^{140}Ce in the precipitation **(a)** unspiked; or spiked with **(b)** engineered
 100 CeO_2 NP, **(c)** paint and **(d)** stain. CeO_2 NP, paint and stain were spiked in the precipitation. For better
 101 readability, only 5 s of data collection were shown, the total acquisition time was 50 s. Measurements
 102 were obtained using SP-ICP-MS with a 50 μs dwell time.

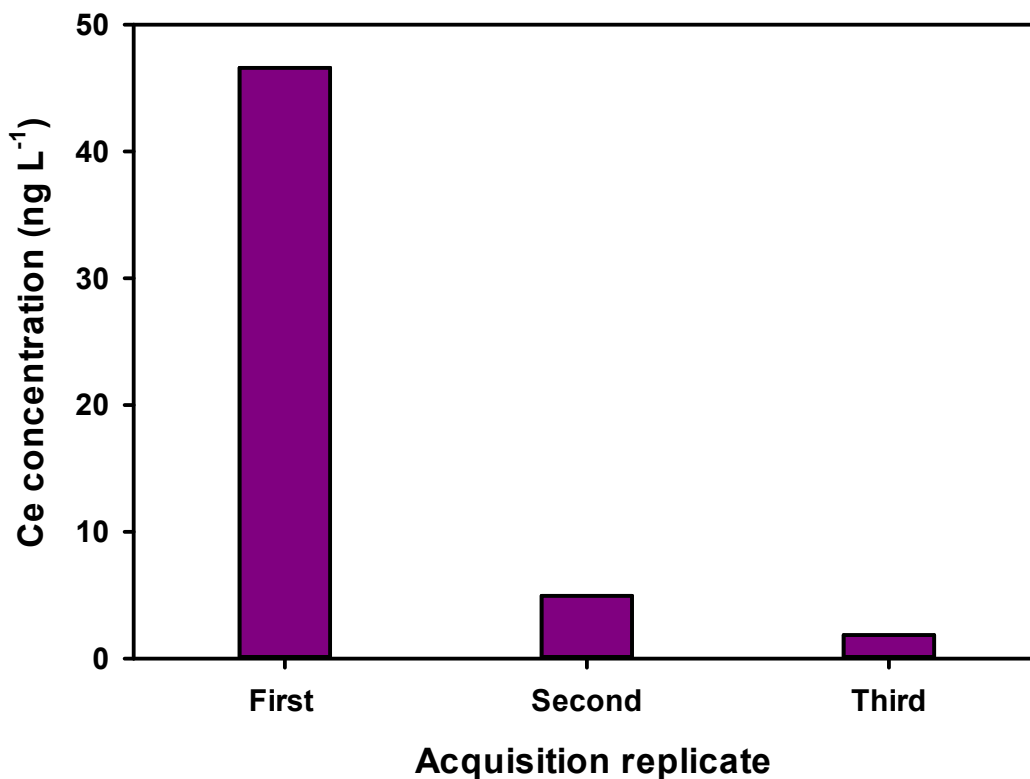
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104 **Table S3.** pH and concentrations of major elements, including total organic carbon (TOC), in an unfiltered
 105 rainwater.

Element	Concentration ($\mu\text{g L}^{-1}$)									pH	
	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Zn		TOC
Rain	4.9 \pm 0.3	3784 \pm 170	0.4 \pm 0.0	5.1 \pm 0.1	221 \pm 11	914 \pm 38	0.5 \pm 0.0	1747 \pm 79	<DL	3040 \pm 46	5.2

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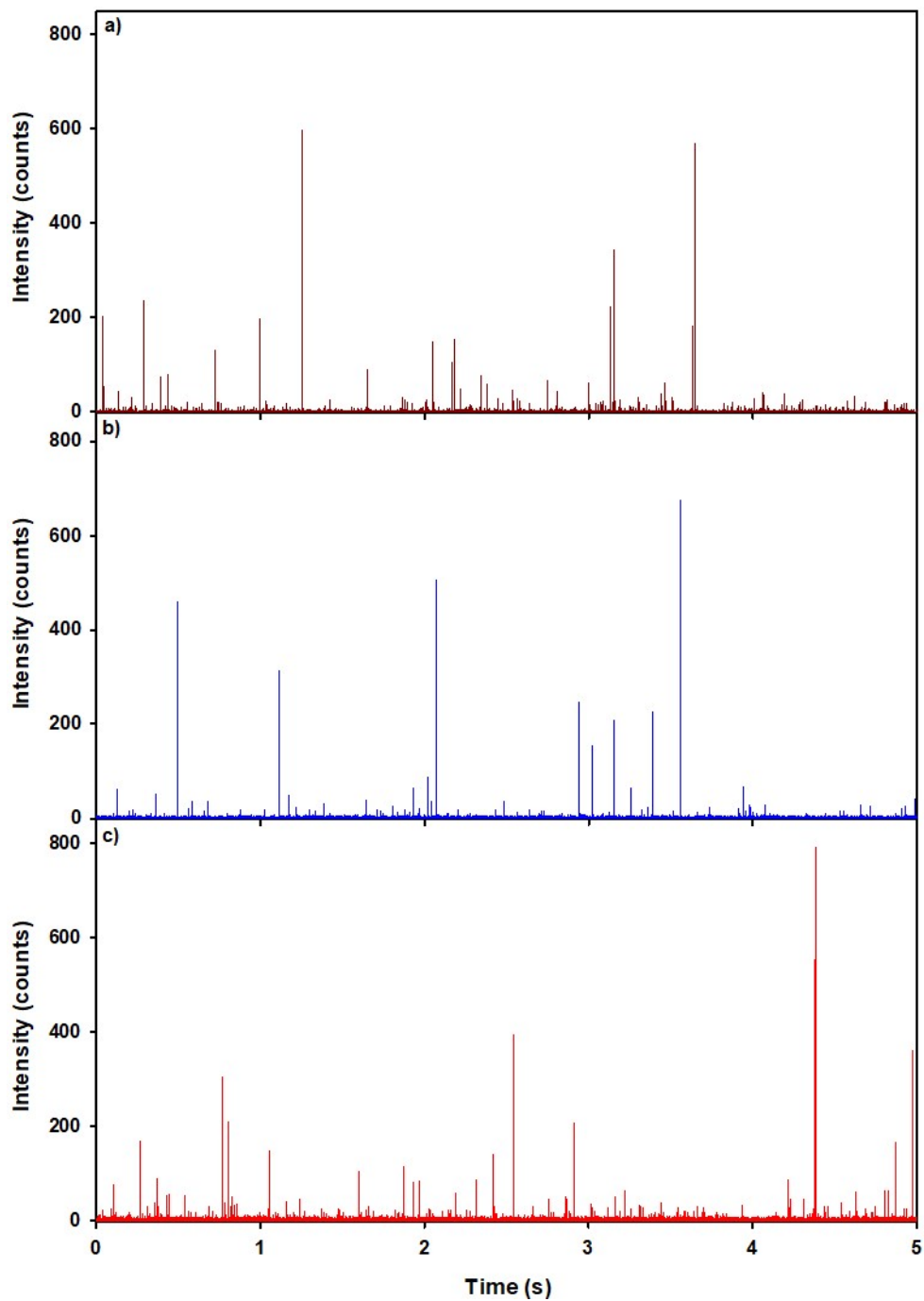
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109 **Figure S13.** Concentration of dissolved Ce measured in successive (triplicate) rinses in 2% HNO₃ following
 110 the analysis of an unfiltered precipitation sample. Measurements were performed using SP-ICP-MS and a
 111 dwell time of 50 μs .

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114 **Figure S14.** Time resolved signal for ^{140}Ce in a filtered precipitation **(a)** without, or with contact with a **(b)**
 115 painted panel, and **(c)** stained panel. For better readability, only 5 s of data collection were shown, the
 116 total acquisition time was 50 s. Measurements were obtained using SP-ICP-MS with a 50 μs dwell time.

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