

1 **Stability and aggregation behavior of metal oxide nanoparticles in natural aqueous**  
2 **matrices**

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4 **Supporting Information**

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15 The supporting information section consists of six pages (A through 5) and includes five  
16 figures.

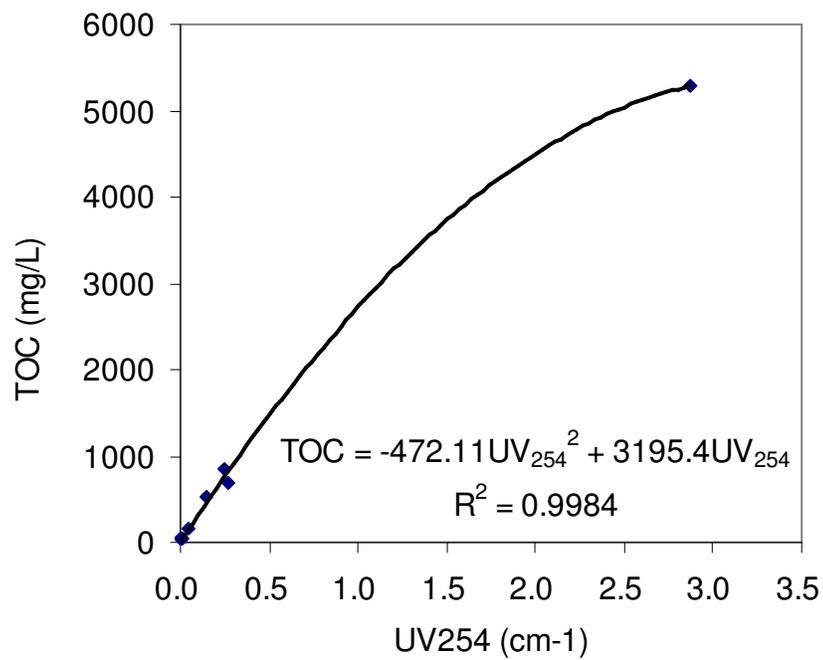
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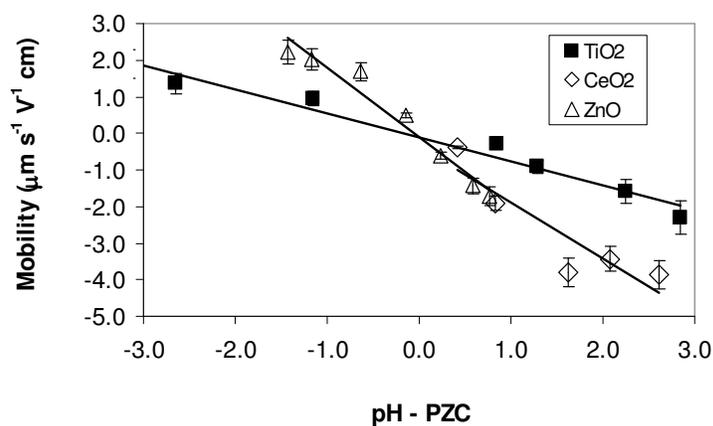


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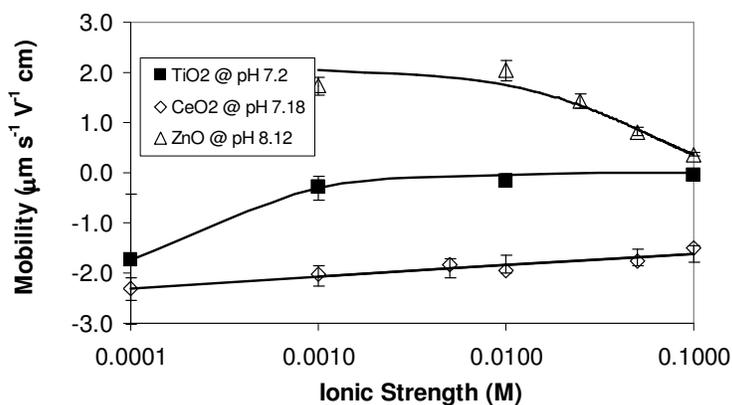
21 **Figure S-1.** Correlation between  $UV_{254}$  and TOC.  $UV_{254}$  was a good predictor for TOC

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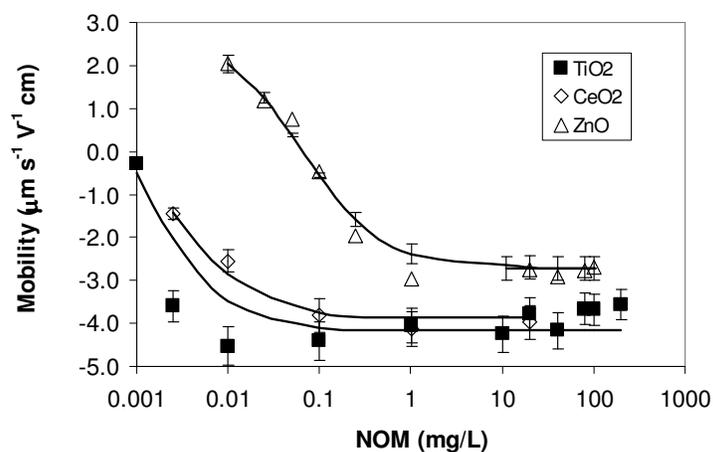
for most of these complex water matrices.



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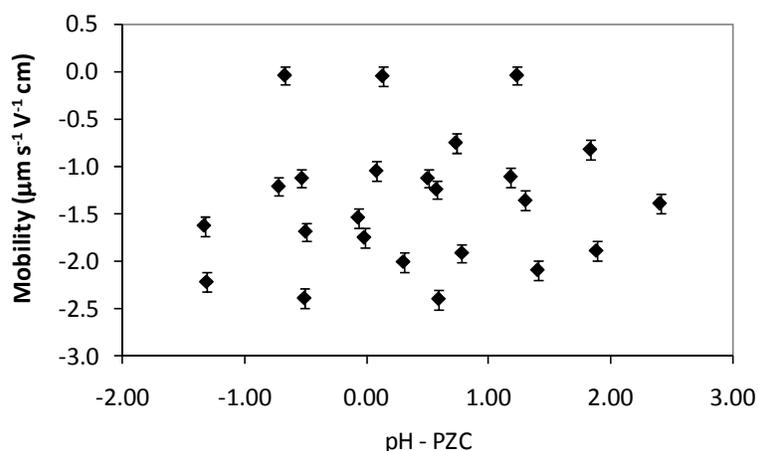


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26 Figure S-2. Electrophoretic mobility of the three metal oxide nanoparticles as a function  
 27 of (a) pH, normalized using pH - PZC; (b) ionic strength at a given pH; and (c) NOM, at  
 28 the same pH as in S-2b and with an ionic strength of 10 mM.

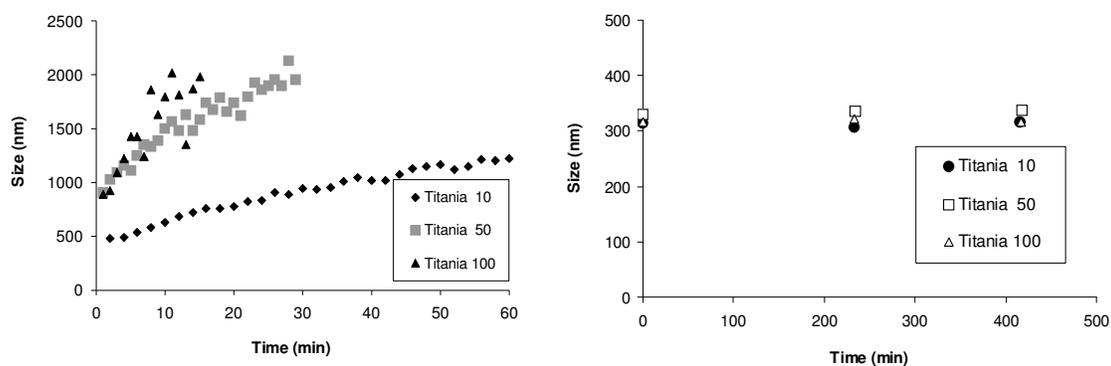


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30 Figure S-3. Electrophoretic mobility of TiO<sub>2</sub>, ZnO and CeO<sub>2</sub> in nine different waters as a  
 31 function of pH (plotted as pH - Point of Zero Charge).

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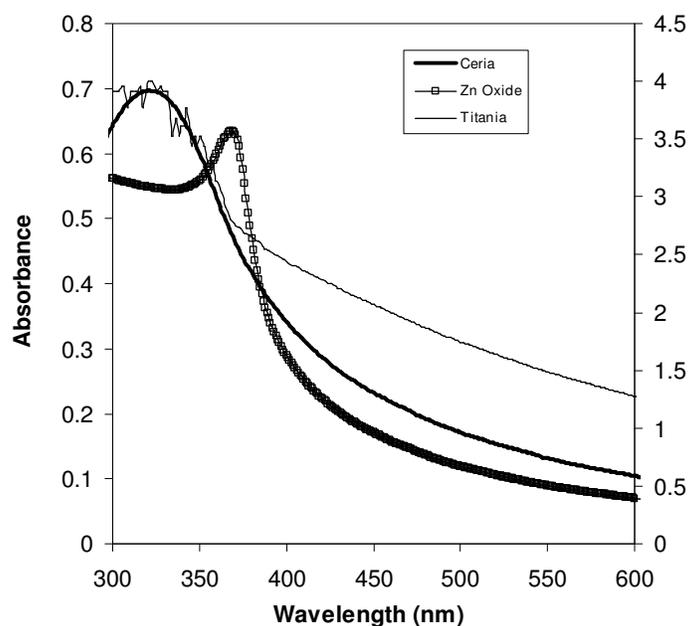
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39 Figure S-4. Dynamic light scattering studies of the aggregation of TiO<sub>2</sub> at 3 different  
 40 initial nanoparticle concentrations (10, 50 and 100 mg L<sup>-1</sup>) (a) in seawater; and (b) in  
 41 freshwater. The average index of polydispersity in seawater was 0.27 for 10 mg L<sup>-1</sup>, 0.37  
 42 for 50 mg L<sup>-1</sup>, and 0.62 for 100 mg L<sup>-1</sup>. For freshwater, the average index of  
 43 polydispersity was 0.27 for 10 mg L<sup>-1</sup>, 0.28 for 50 mg L<sup>-1</sup>, and 0.30 for 100 mg L<sup>-1</sup>.

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46 Figure S-5. UV-Vis spectra for the three metal oxide nanoparticles. Left y-axis for CeO<sub>2</sub>  
 47 and ZnO, right y-axis for TiO<sub>2</sub>.

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49 **Attachment efficiency calculations**

50 The attachment efficiency of two colloids can be determined from their rate of  
 51 aggregation [35, 36] or by measuring the effect of aggregation, which is the  
 52 sedimentation of the aggregates [41]. As the nanoparticles aggregate and settle out of the  
 53 suspension, the optical absorbance decreases. Thus, one can measure the change optical  
 54 absorbance with time, which can be related to the normalized nanoparticle concentration  
 55  $C/C_0$ , where  $C$  is the concentration in time, and  $C_0$  is the initial concentration (i.e. the  
 56 initial absorbance at time 0). The sedimentation rate is then  $d(C/C_0)/dt$ . As can be  
 57 observed in Figure 2, under conditions that lead to fast sedimentation, there is an initial  
 58 high rate of sedimentation which decreases as the number of nanoparticles and small  
 59 aggregates in solution decreases. Thus, we consider only the initial rate up to a 5%

60 decrease in normalized concentration, within the first few minutes, as the rate of  
61 sedimentation of interest for understanding nanoparticle attachment, just as is done using  
62 the rate of aggregation of nanoparticle to doublets [6]. For the more stable conditions (e.g.  
63 Figure 4, in freshwater), we use the initial rate of sedimentation up to 60 min, since in  
64 some cases the dispersion is so stable that we do not observe any settling in the first  
65 minutes. To determine the apparent attachment coefficients,  $\alpha$ , we consider the rate of  
66 sedimentation divided by:

$$67 \quad \alpha = k_{sed,i}/k_{sed,seawater} \quad \text{(Equation S-1)}$$

68 where  $k_{sed,i}$  is the sedimentation for the  $i^{\text{th}}$  given condition (e.g. freshwater, groundwater)  
69 and  $k_{sed,seawater}$  is the rate in the fastest sedimentation conditions (i.e. seawater in all cases).  
70 By this definition, we assign an attachment coefficient of 1 to seawater, and all others  
71 range from 0 to 1. The rate of aggregation in seawater is essentially the diffusion-limited  
72 aggregation rate,  $k_{Smol}$ , also denominated the Smoluchowski aggregation rate [44],  $k_{Smol} =$   
73  $8k_B T/3\mu$ , where  $k_B$  is the Boltzmann constant =  $1.38066 \times 10^{-19}$  J K<sup>-1</sup>;  $T$  is the absolute  
74 temperature; and  $\mu$  is the solution's viscosity. The sedimentation rate at 10 mg L<sup>-1</sup> was  
75 chosen for calculating  $\alpha$  since it is not as influenced by the collision frequency as at  
76 higher concentrations.

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