Monitoring Fate and Behaviour of Nanoceria under relevant Environmental Conditions

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Introduction

Wagner et al. *Angew. Chem. Int. Ed.* **2014,**

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Introduction cont…

Table 1: Global production volumes of ENMs

ENMs Type	ENM production (tons per year)								
	World wide	US	Europe	Switzerland	Germany	Australia	China	Japan	Korea
TiO_2	**>60,000**	7800-38000	55-3000	435	400	~40,000	**2000**	**1250**	**>1600**
ZnO	**>1,400,000**	>1000	5.5-28,000	70	>500	>15	**>1000**	**480**	_
CeO_2	**0.55-2800**	35-700	>55	_	_	>5	_	_	_
SiO_2	**55-55,000**	_	88-55,000	75	_	<0.01-50	**>3000**	**13,500**	_
Fullerence	**0.15-80**	2-80	0.6-5.5	_	_	_	_	**2**	_
Carbon nanotubes	**>4065**	55-1101	180-550	1	>260	>3	**>560**	**>500**	**7-90**
Quantum dots	**0.6-5.5**	_	0.6-5.5	_	_	_	_	_	_
Nano Ag	**>550**	2.8-20	0.6-55	3.1	>8	_	**>200**	_	**~390**

Nanomaterials report (2008), Schmid and Reidiker (2008), Park et al. (2009/2011), Wijnhoven et al. (2009), Batley and McLaughlin (2010), Carbon nanotubes report (2011), Hendrin et al,(2011), Zhang et al. (2011), Fries and Simko (2012), Piccinno et al. (2012) Research and Markets (2012), Korea IT new (2013)

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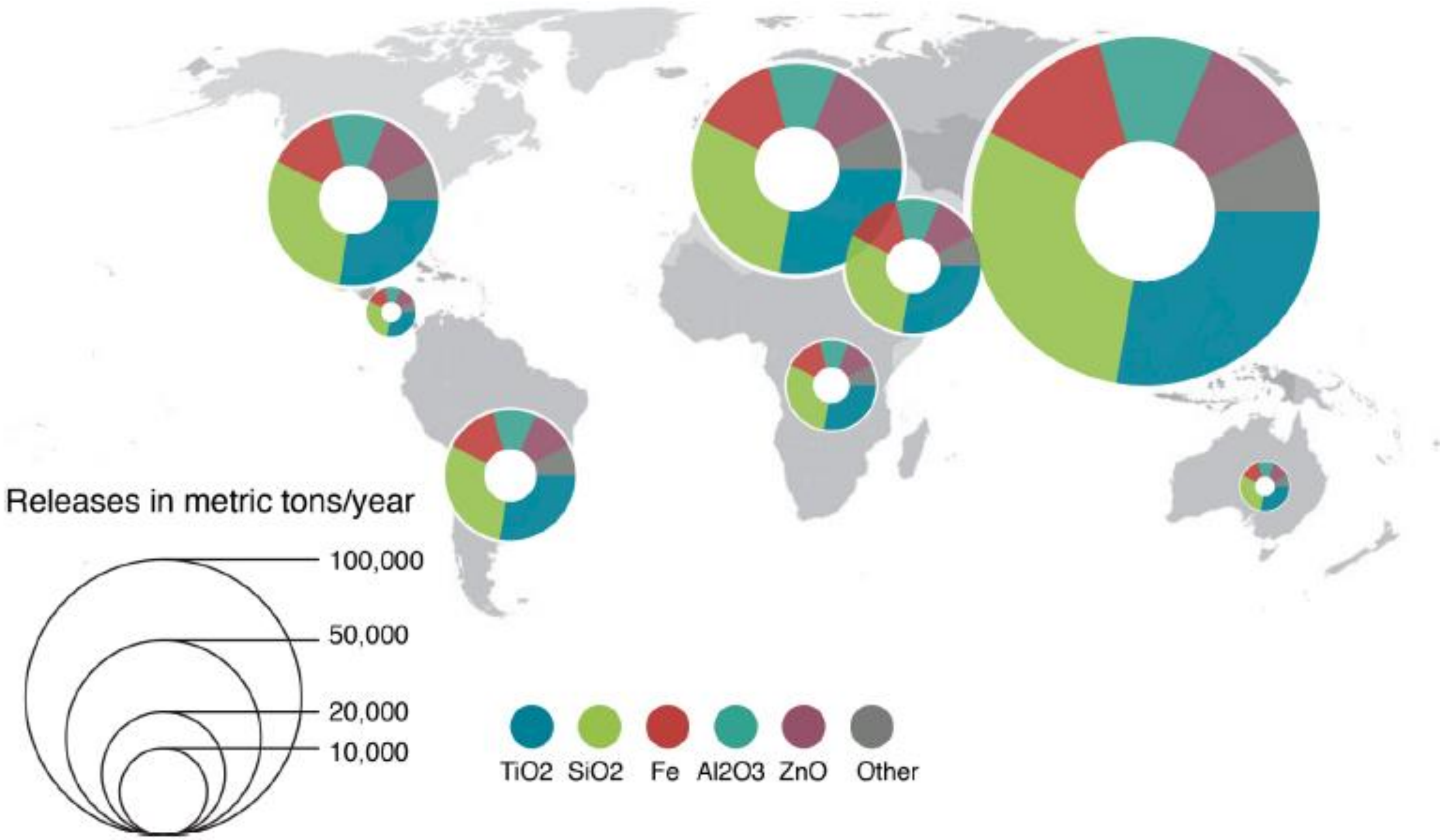
Global Distribution of ENMs Type Release per Continent to air, water, soil, and landfills



Keller and Lazareva, EST, 2013

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Motivation for the study

- Why the need:
  - There's a dramatic increase in production of ENMs
  - Concerns over their release in the environment
  - Establish pathways for ENMs fate, and transport in aquatic systems
- Impact and relevance
  - Enhance collective understanding of ENMs fate, behaviour, and effects in environmental systems to support *safe, responsible and sustainable exploitation of nanotechnology-driven capabilities*

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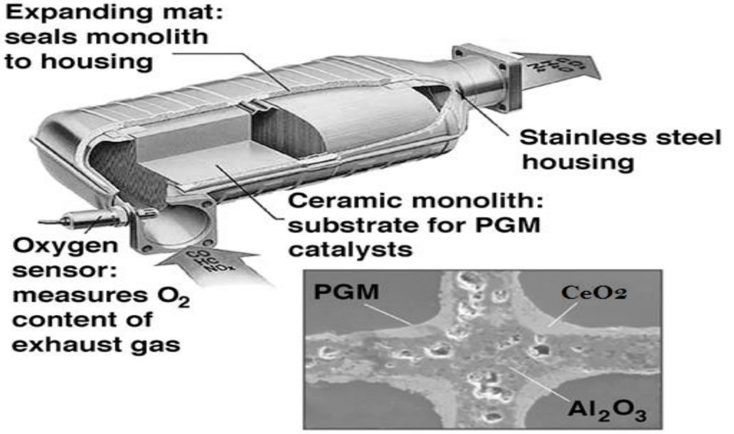
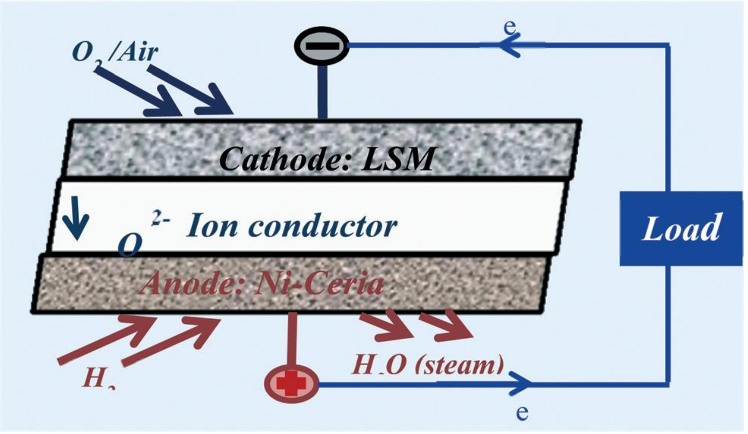
Nanoceria Applications





Closeup of the gridwork in a catalytic converter.

The increasing applications will inevitably lead to CeO2 release into the environment, which will impose risks on humans and ecosystems. Listed one of the 14 ket ENMs of focus by OECD.

Closeup of the Gridwork in a Catalytic Converter. Digital image. Reddit. Reddit Inc., 2014. Web. 29 Oct. 2014. <www.reddit.com/related/esn5a/platinum_group_metals_ruthenium_rhodium_palladium/>.

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Other applications of nanoceria are:

- Biomedical applications such as its use as an antioxidant (Chen *et al*. 2013)
- UV-Shielding (Dao *et al*. 2011), e.g. application as a sunscreen component (Zholobak *et al*. 2011)
- *Used in toner formulation (Bello et al. 2013)*
- Used in catalysts in petroleum refining, in the fluid catalytic cracking process (FCC) (Global Market for Nanomaterials, 2012)

S. Chen, Y. Hou, G. Cheng, C. Zhang, S. Wang and J. Zhang,Biol. Trace Elem. Res., 2013
N. N. Dao, M. D. Luu, Q. K. Nguyen and B. S. Kim, Adv. Nat. Sci.: Nanosci. Nanotechnol., 2011
N. M. Zholobak, V. K. Ivanov, A. B. Shcherbakov,A. S. Shaporev, O. S. Polezhaeva, A. Y. Baranchikov,N. Y. Spivak and Y. D. Tretyakov, J. Photochem. Photobiol., B,2011
D. Bello, J. Martin, C. Santeufemio, Q. Sun, K. L. Bunker,M. Shafer and P. Demokritou, Nanotoxicology, 2013
The Global Market for Nanomaterials 2002–2016: Production volumes, revenues and end user markets, Future Markets, Inc.,http://www.futuremarketsinc.com, (accessed Jan 29, 2013),2012.

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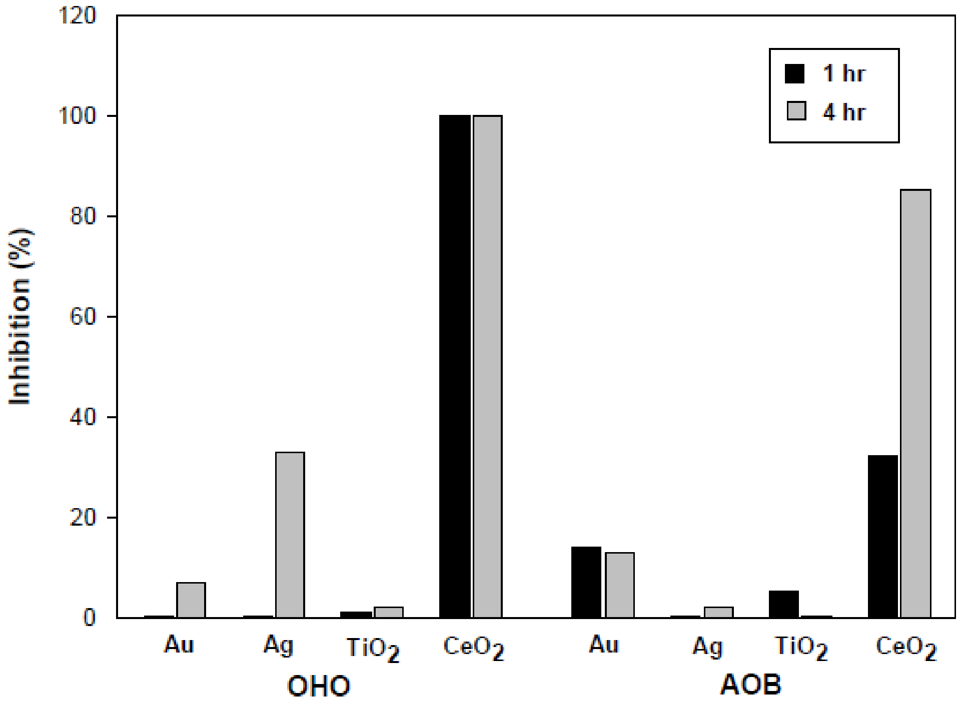
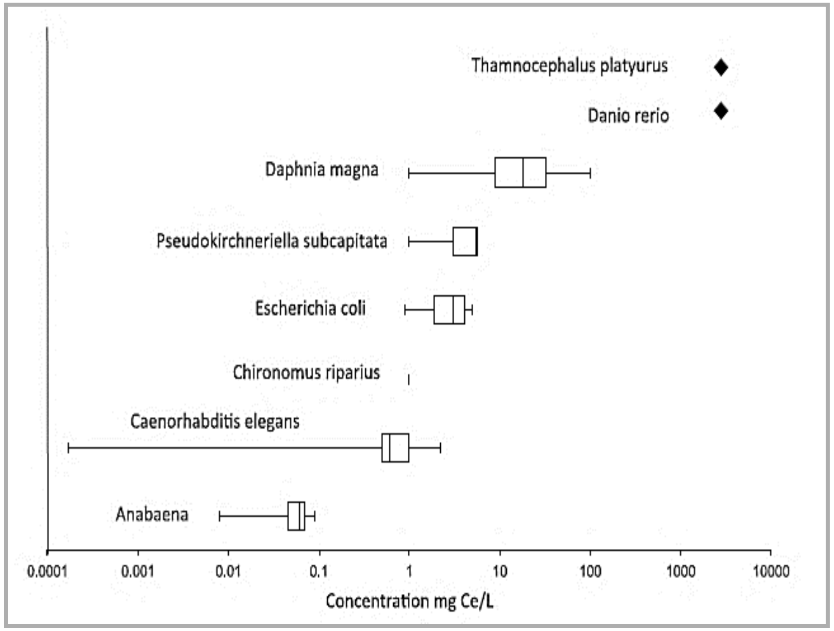
Toxicity studies of CeO_2 in environmental systems



Garćia et al. J. Hazard. Mat., 2012



Collin et al. Environ. Sci. Nano. 2014

ordinary heterotrophic organisms (OHO) and ammonium oxidising bacteria (OAB)

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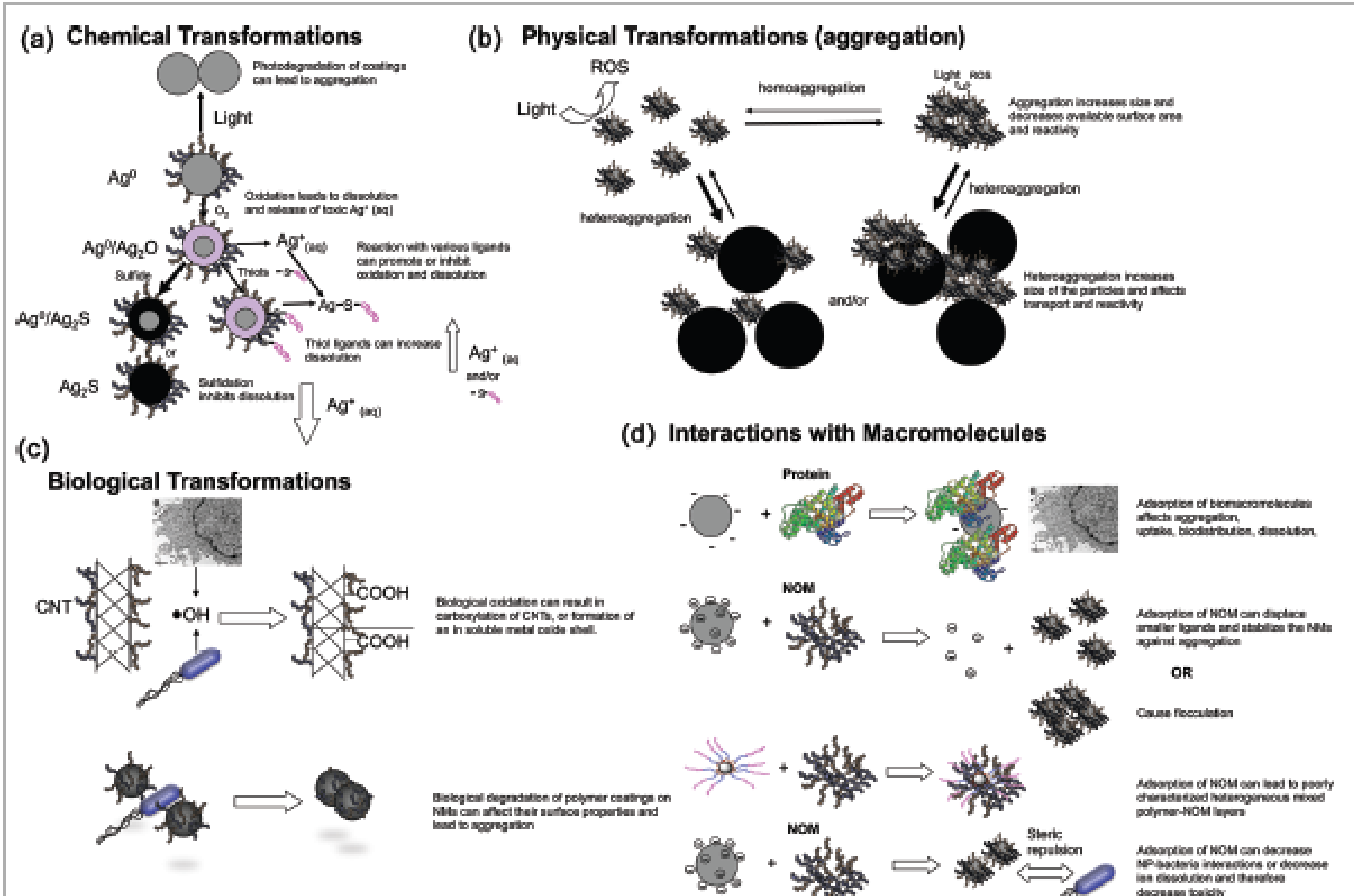
Likely scenarios of ENMs fate and transformation in environment



Lowry et al.,EST, 2012

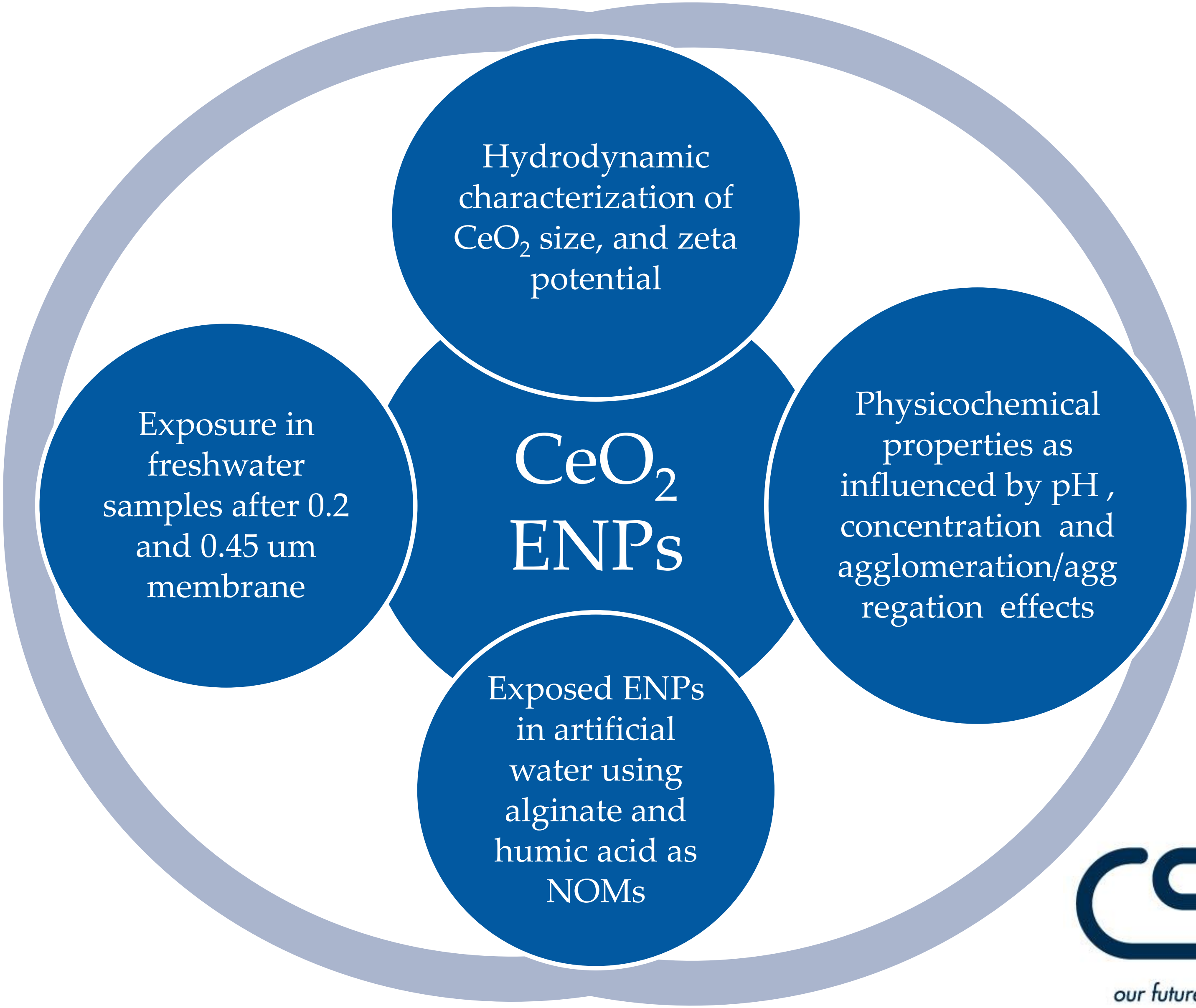
Objectives

- To investigate the effect of abiotic factors: pH and natural organic matter (NOMs)

- To investigate the stability in freshwater system with respect to aggregation/agglomeration

Data from studies chiefly aided to elucidate fate and behavioural of nanoceria in aquatic systems

Experimental Design



Freshwater characterization data

Parameter	Value (stdev.)
pH	7.05-7.54 (0.15)
DOC mg/L	3.2-3.77 (0.17)
Na^{+} mg/L	13 (0.03)
Ca^{2+} mg/L	10.67 (0.47)
Mg^{2+} mg/L	7.93 (0.05)
SO_4^{2-} mg/L	7.97 (0.17)
Cl^{-} mg/L	0.02 (0.005)

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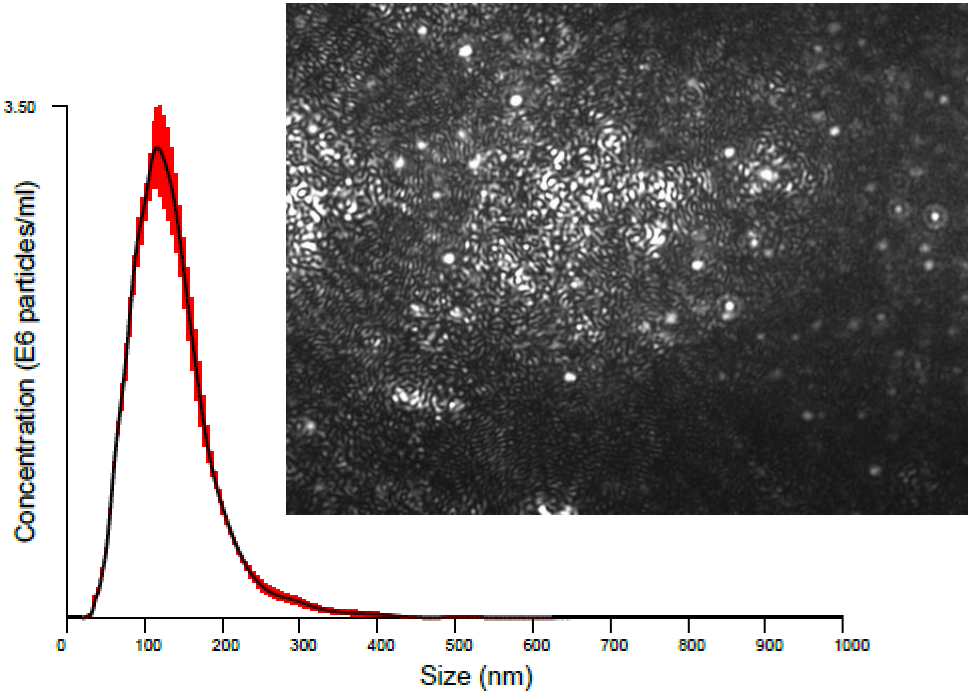
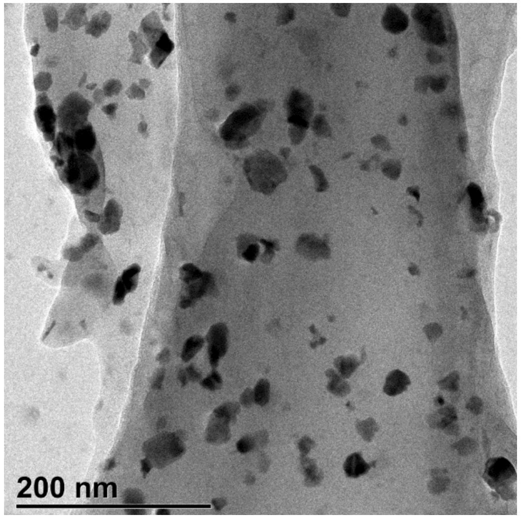
Characterization of CeO_2 NPs



Averaged Size / Concentration
Red error bars indicate +/- 1 standard error of the mean



Av. Size= 25 nm

Method	Size (nm)	Zeta potential (mV)
NTA	117 (±3.6)	11.98 (1.5)
Zetasizer	136.7 (±5.5)	10.4 (0.36)

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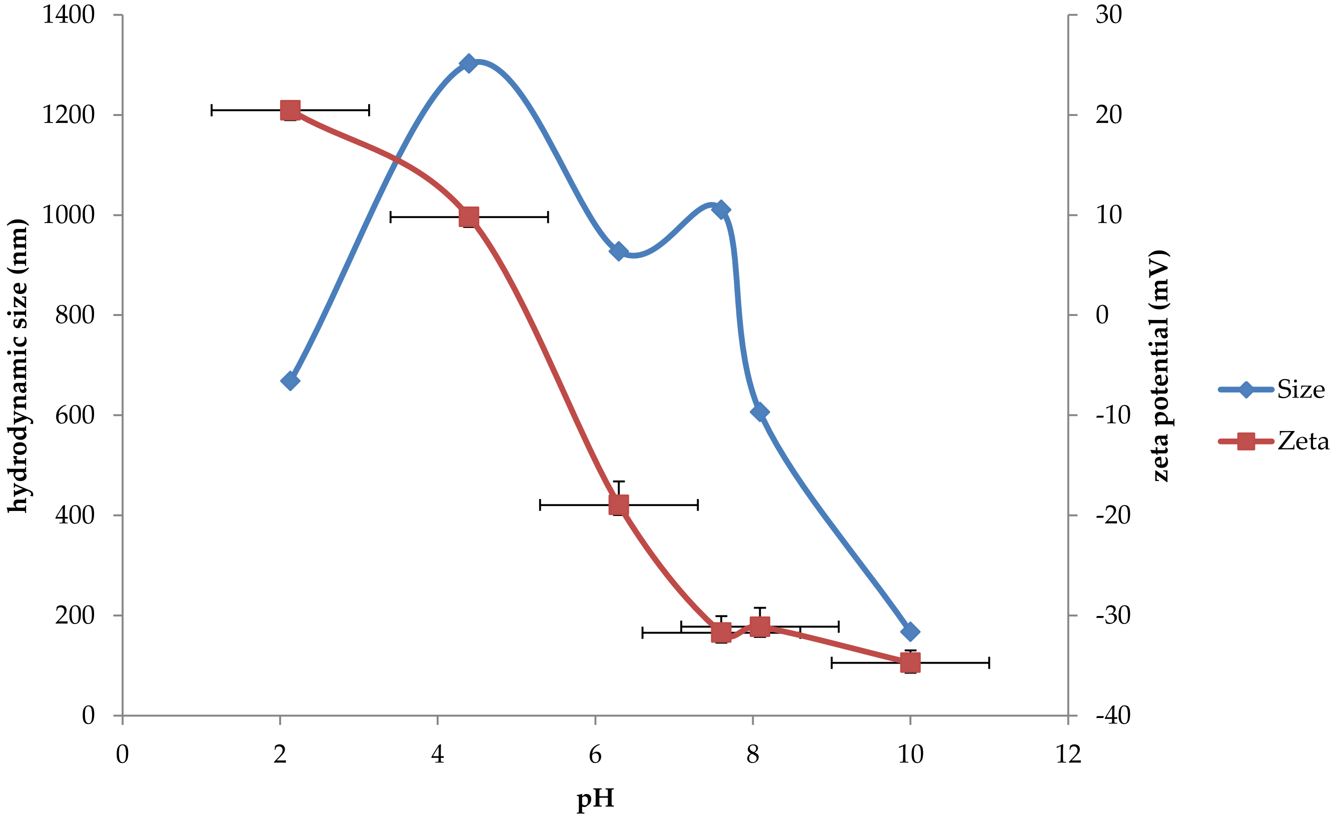
Effect of pH



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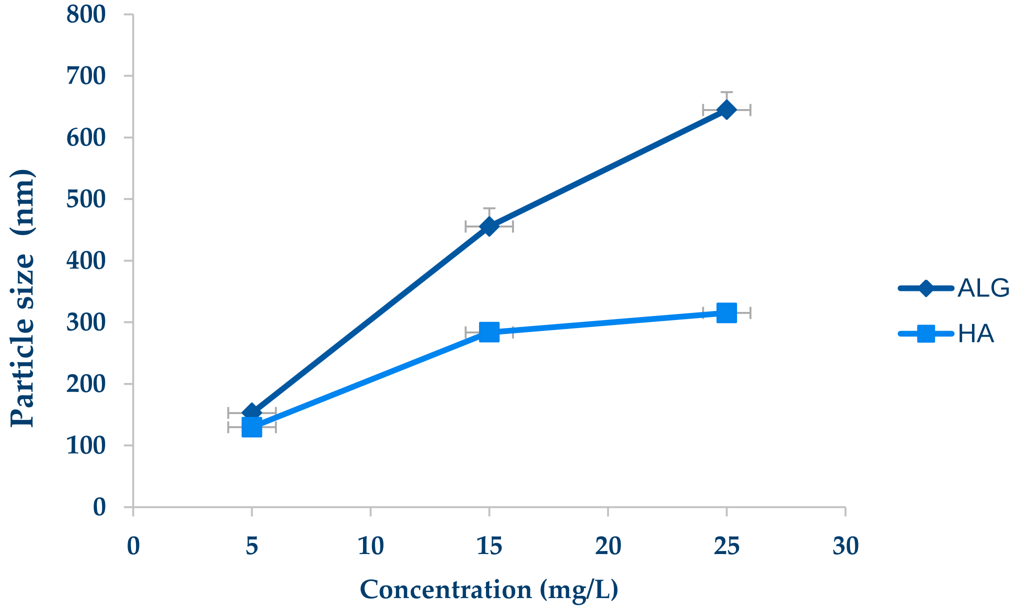
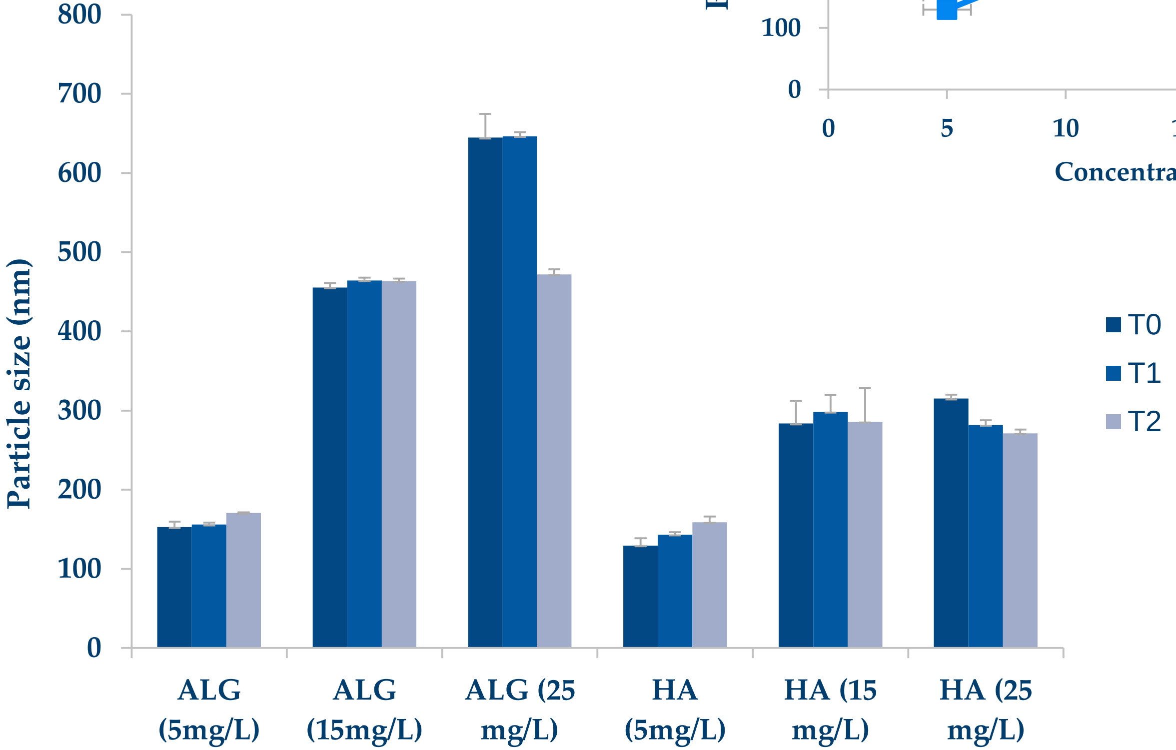
Effect of NOM types on size of CeO_2NPs





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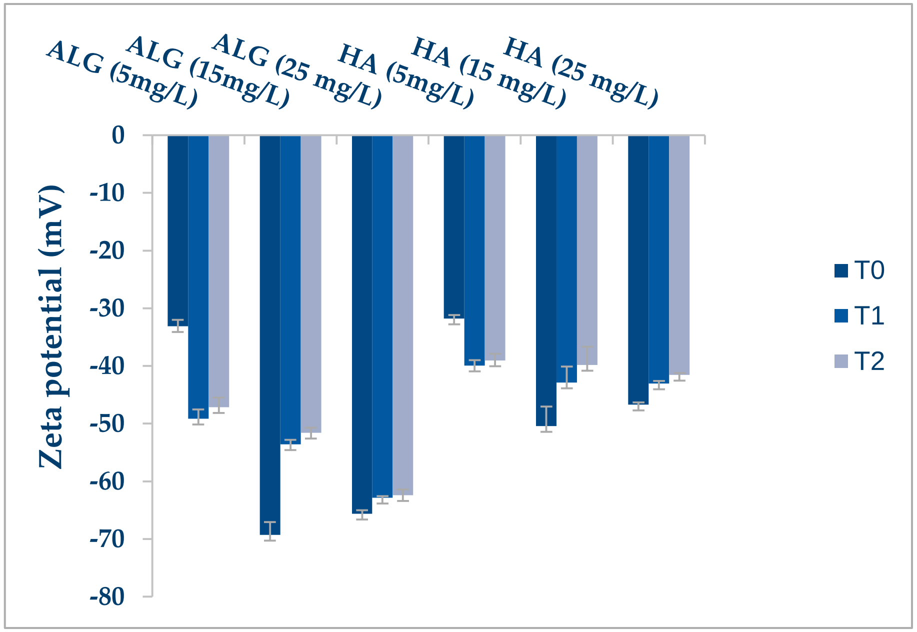
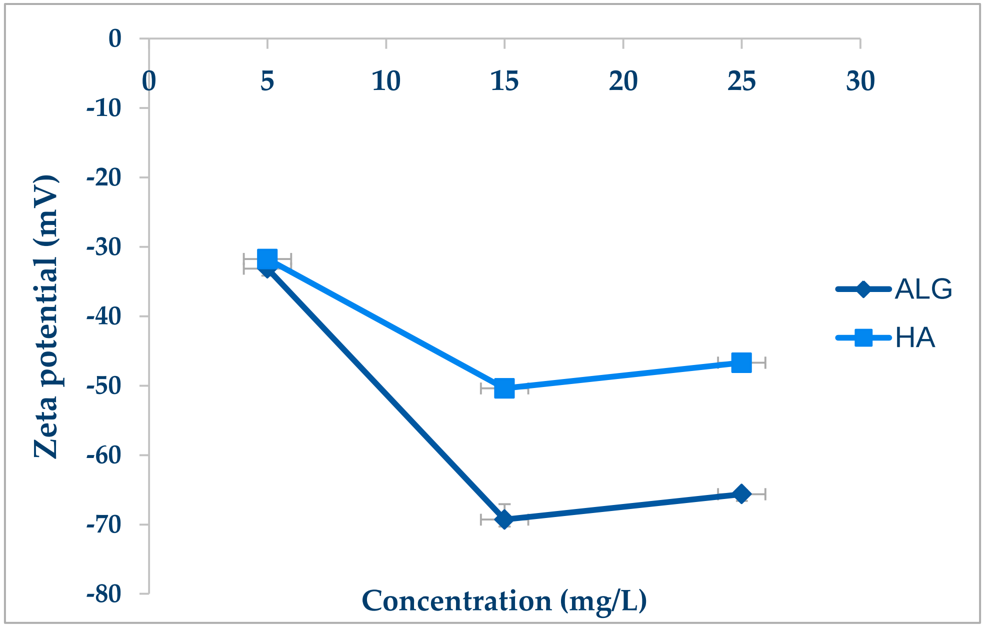
Effect of NOM on Zeta Potential





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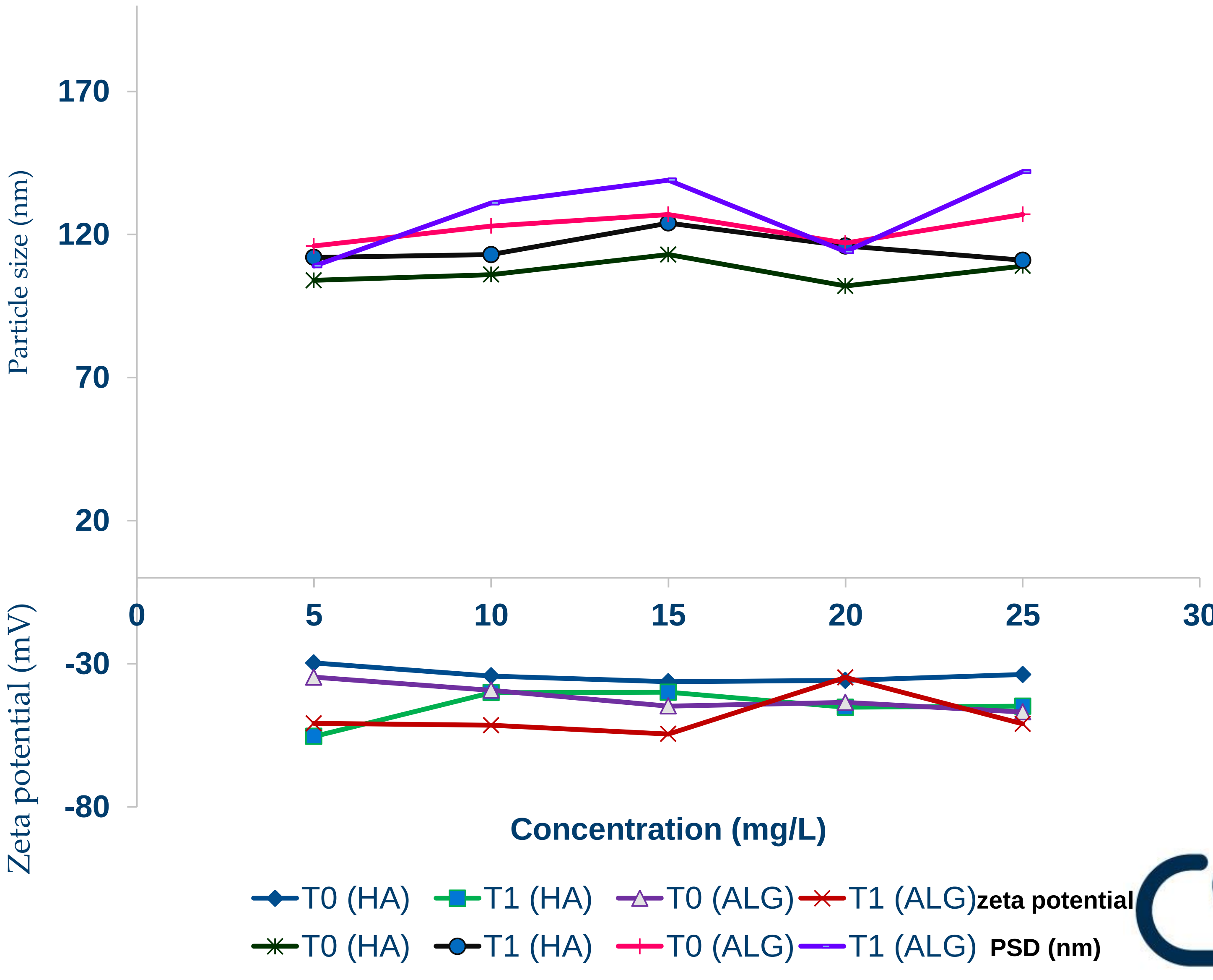
NTA results



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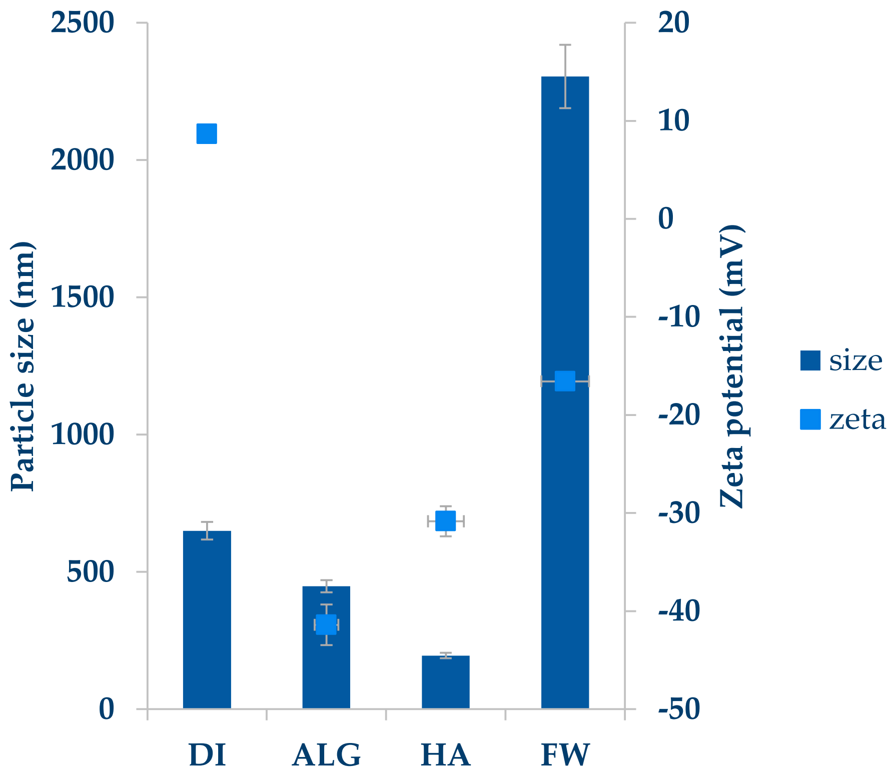
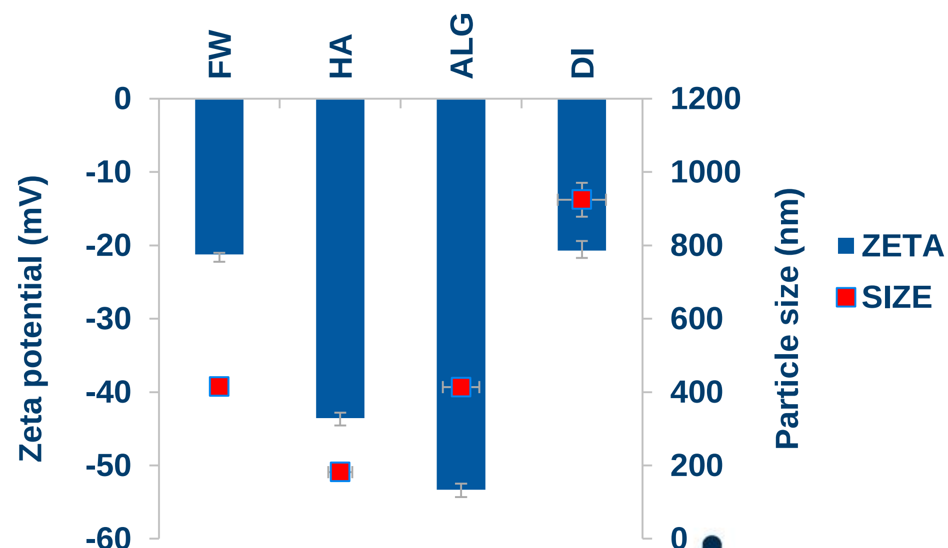
Behaviour of CeO_2NPs along pH_{PZC} range

Sample	pH	Size (nm)	Zeta potential (mV)
control	5.99	158 (±11.9)	8.68
	4	104 (±3)	12.05
	5	122 (±4.4)	9.58
FW (T0)	7.34	99 (±2.4)	-18.98
FW (T1)	7.58	108 (±4)	-27.5





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Summary

- CeO_2 NPs are highly unstable and tend to settle out of aqueous phase
- NOM show to stabilise the NPs though significant agglomeration occurs
- In freshwater, aggregation/agglomeration occurs still at nano scale depending on the conditions

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Future work

- Monitor aggregation and agglomeration rates at longer duration period and whether deagglomeration/deaggregation is possible for CeO_2 NPs
- Study dissolution rates
- Stabilization and surface functioning of the NPs

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Acknowledgements

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