How water chemistry determines the risk of metallic engineered nanoparticles in aquatic ecosystems: nAg and nZnO case study

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6TH SETAC AFRICA– 2-3 SEPTEMBER 2013

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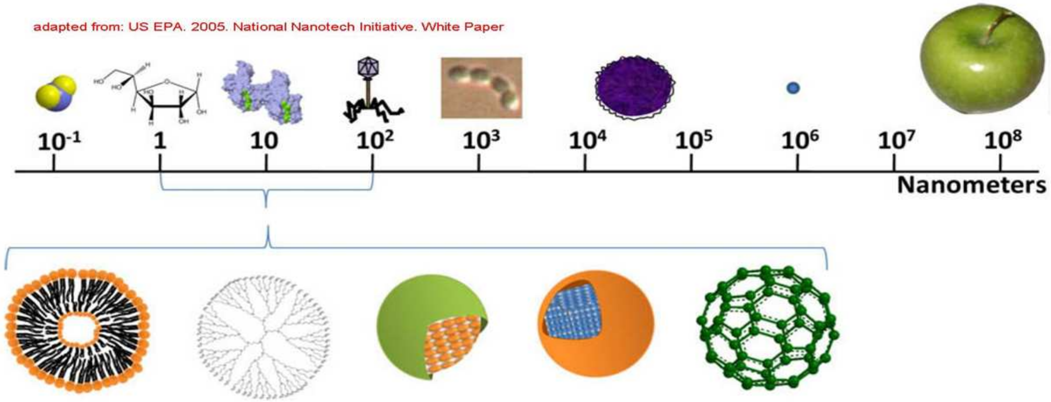


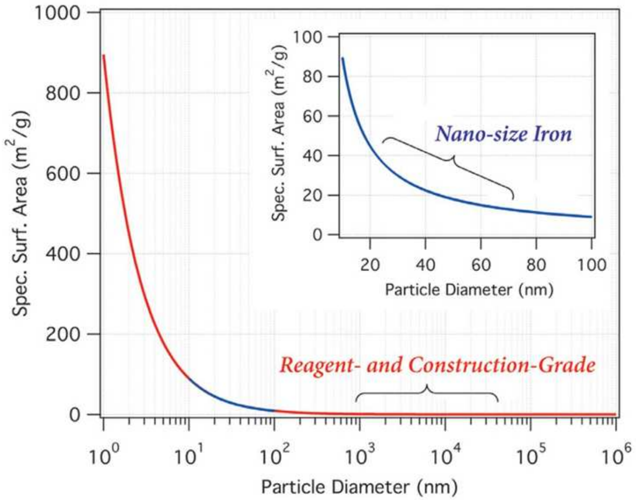


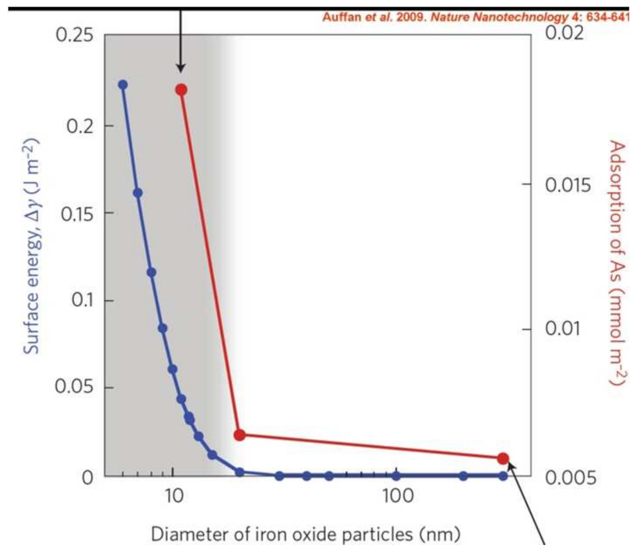
Fig. 2 Particle surface area calculated from diameter assuming spherical geometry and density 6.7 g/cm³ (based on the average of densities for pure Fe^0 *and* Fe_3O_4*).* Tratnyek and Johnson. 2006. *NanoToday* 1(2): 44-48

reactivity

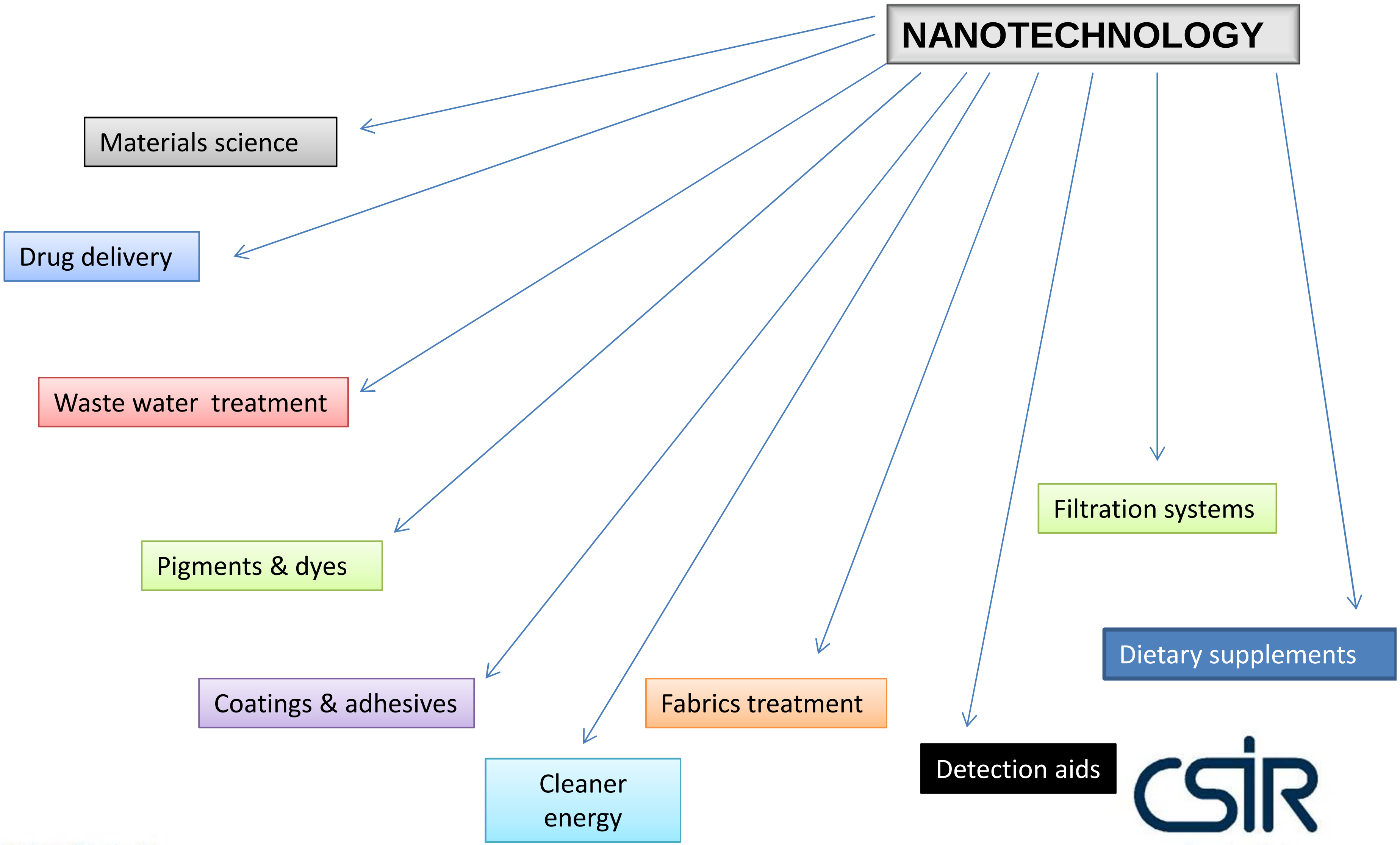
solubility

conductivity

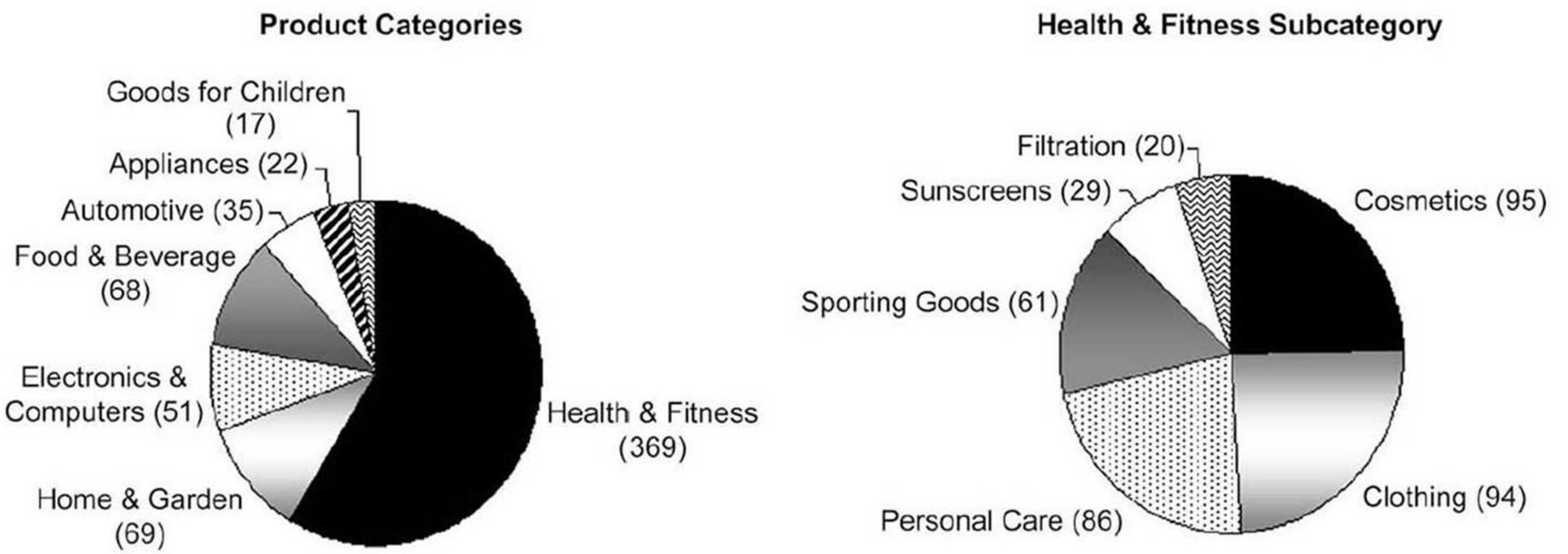
strength



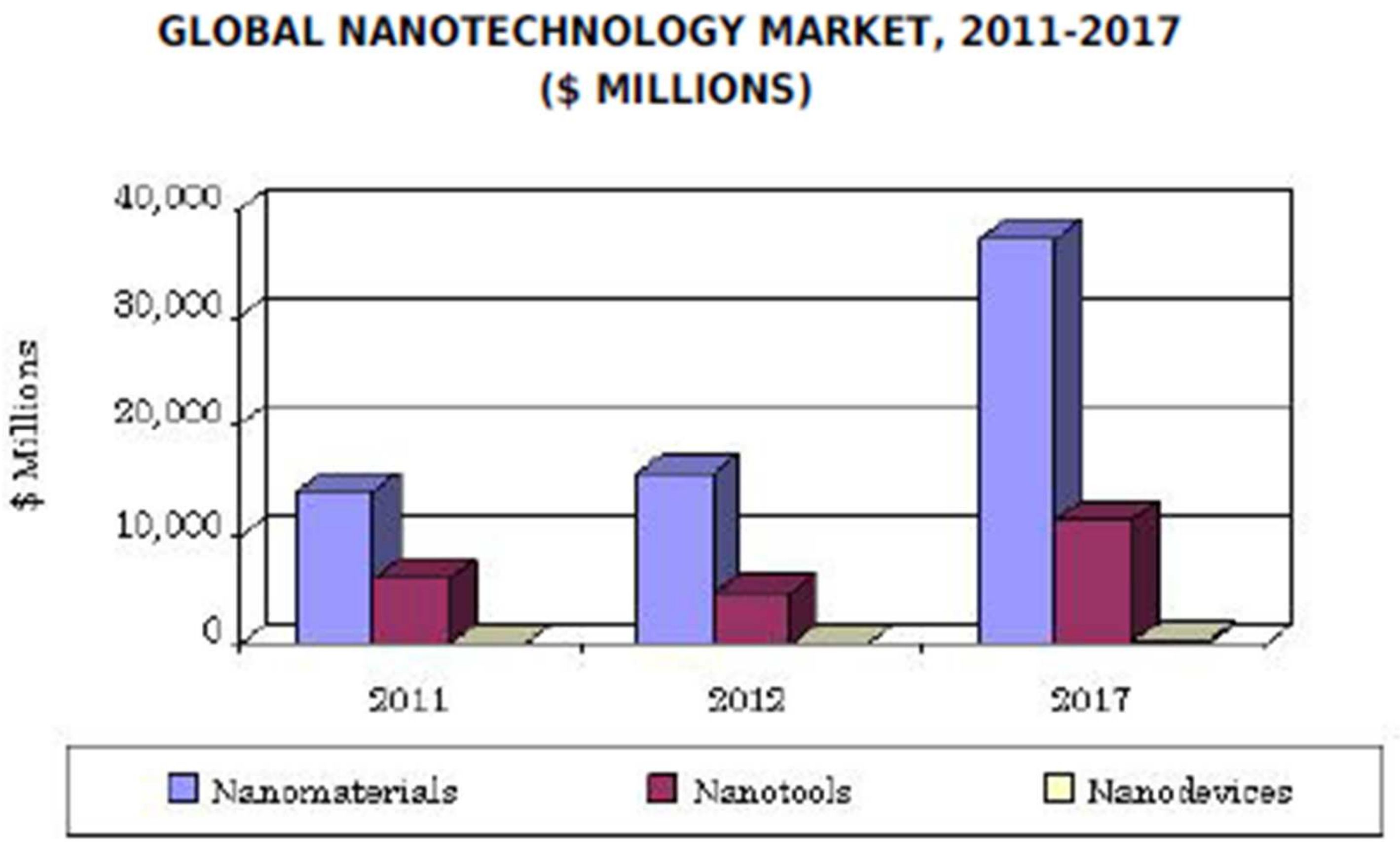
APPLICATIONS



Daily and domestic reach



Consumer products currently available that contain nanomaterials. Adapted from the Woodrow Wilson Database in Jan 2009 (http://www.nanotechproject.org).


GLOBAL NANOTECHNOLOGY MARKET, 2011-2017
($ MILLIONS)
$ Millions
40,000
30,000
20,000
10,000
0
2011
2012
2017
Nanomaterials
Nanotools
Nanodevices

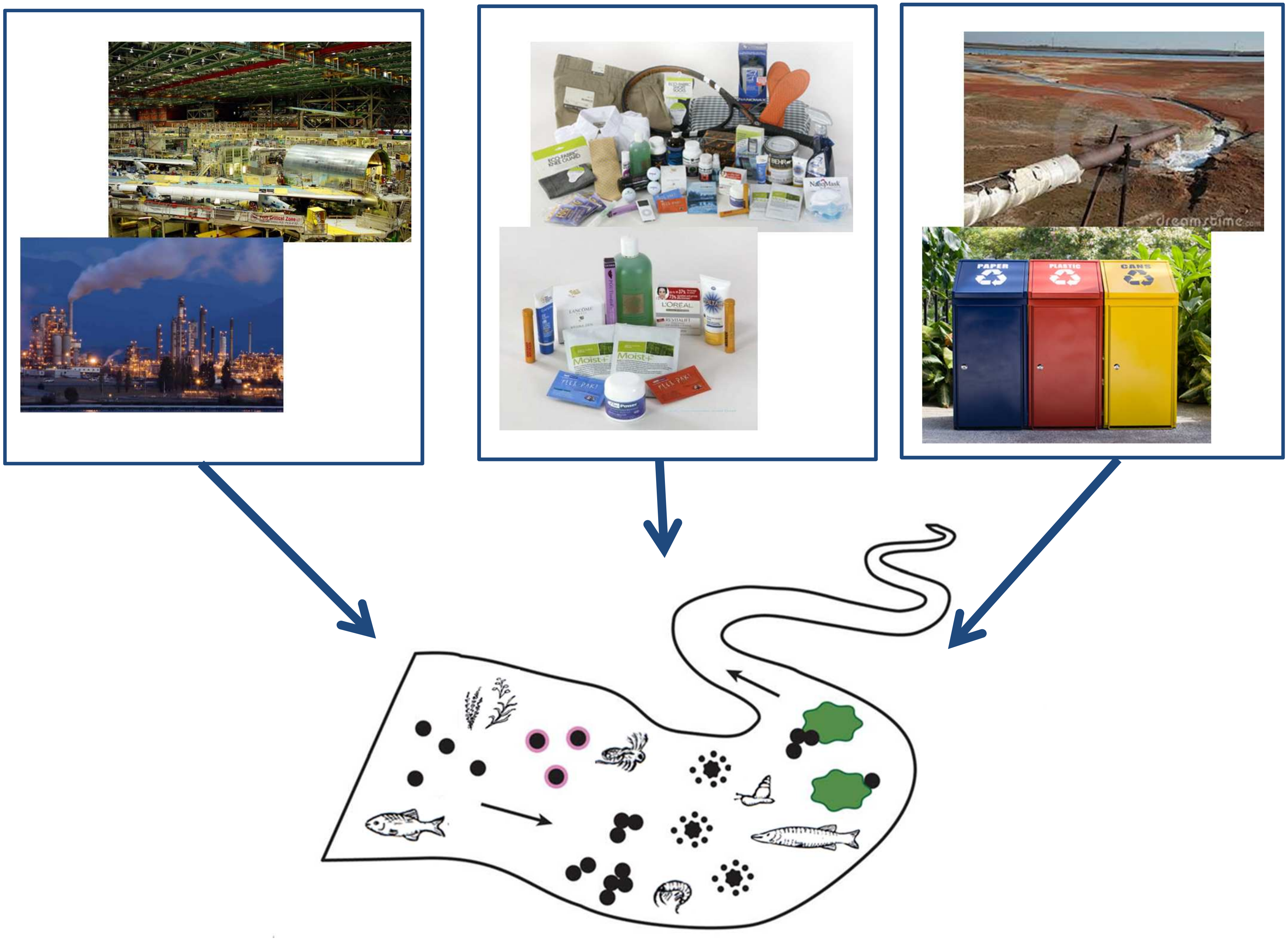
GLOBAL NANOMATERIALS SALES BY TYPE, THROUGH 2017
($ MILLIONS)

Nanomaterial Type	2011	2012	2017	CAGR% 2012-2017
Nanoscale thin films	9,356.1	10,835.7	24,553.4	17.8
Solid nanoparticles	2,374.9	2,504.3	6,422.7	20.7
Nanostructured monolithics	1,485.1	1,596.5	3,566.8	17.4
Nanocomposites	855.2	986.5	2,673.3	22.1
Nanotubes and other hollow nanoparticles*	1.6	1.8	111.3	128.2
Total	14,072.9	15,924.8	37,327.5	18.6

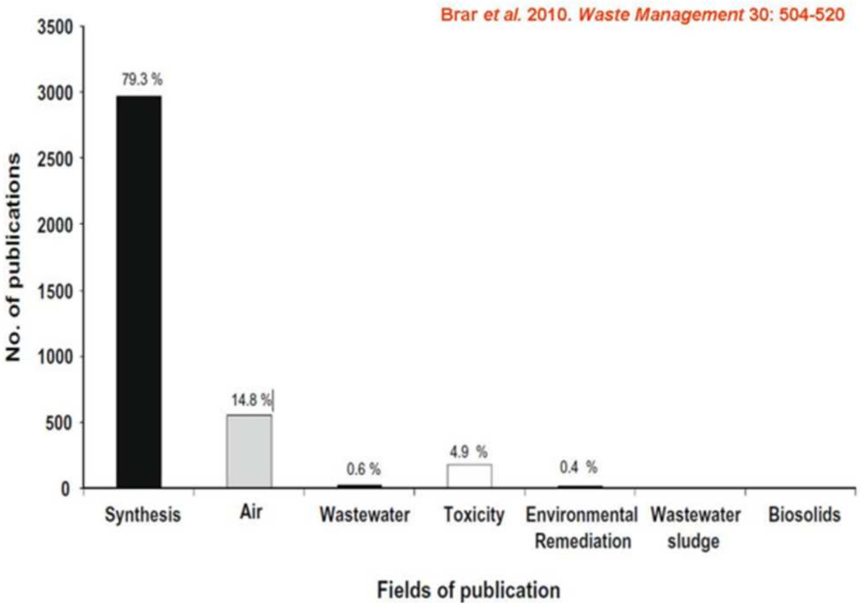
*Excluding nanotube composites, which are included in Nanocomposites segment.

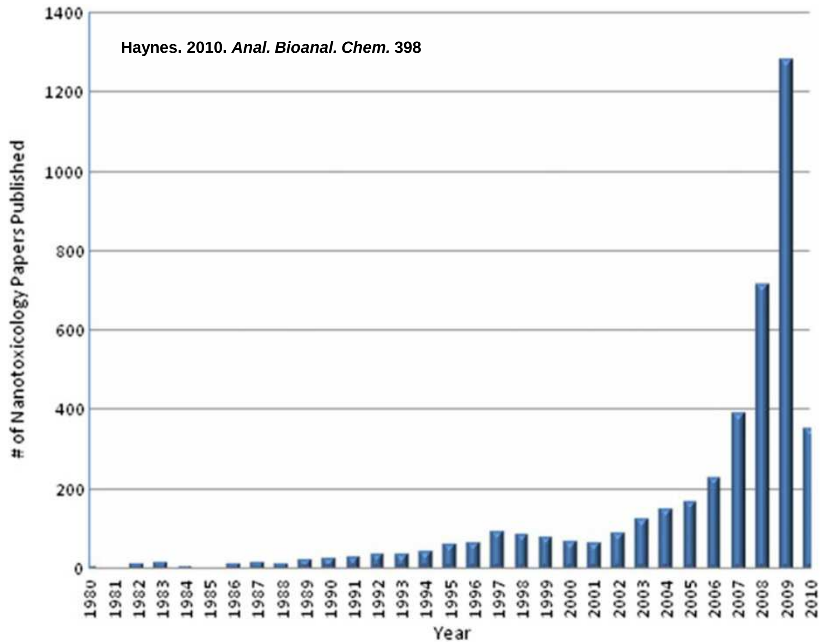
Production of nanoparticles from different sources and respective applications.

Source	Type of nanoparticle	Quantity used in terms of tons	Application/uses
Metals and alkaline earth metals	Ag	High	Antimicrobials, paints, coatings, medical use, food packaging
	Fe	High	Water treatment
	Pt group metals	High	Catalysts
	Sn	Unknown	Paints
	Al	High	Metallic coating/plating
	Cu	Unknown	Microelectronics
	Zr	High	
	Se	Low	Nutraceuticals, health supplements
	Ca	Low	Nutraceuticals, health supplements
	Mg	Low	Nutraceuticals, health supplements
Metal oxides	TiO_2	High	Cosmetics, paints, coatings
	ZnO	Low	Cosmetics, paints, coatings
	CeO_2	High	Fuel catalyst
	SiO_2	High	Paints, coatings
	Al_2O_3	Low	Usually substrate bound, paintings
Carbon materials	Carbon black	High	Substrate bound, but released with tyre wear
	Carbon nanotubes	Medium–High	Used in a variety of composite materials
	Fullerenes (C60-C80)	Medium–High	Medical and cosmetics use
Miscellaneous	Nanoclay	High	Plastic packaging
	Ceramic	High	Coatings
	Quantum dots	Low	Different compositions
	Organic nanoparticles	Low	Vitamins, medicines, carriers for medicines and cosmetics, food additives and ingredients

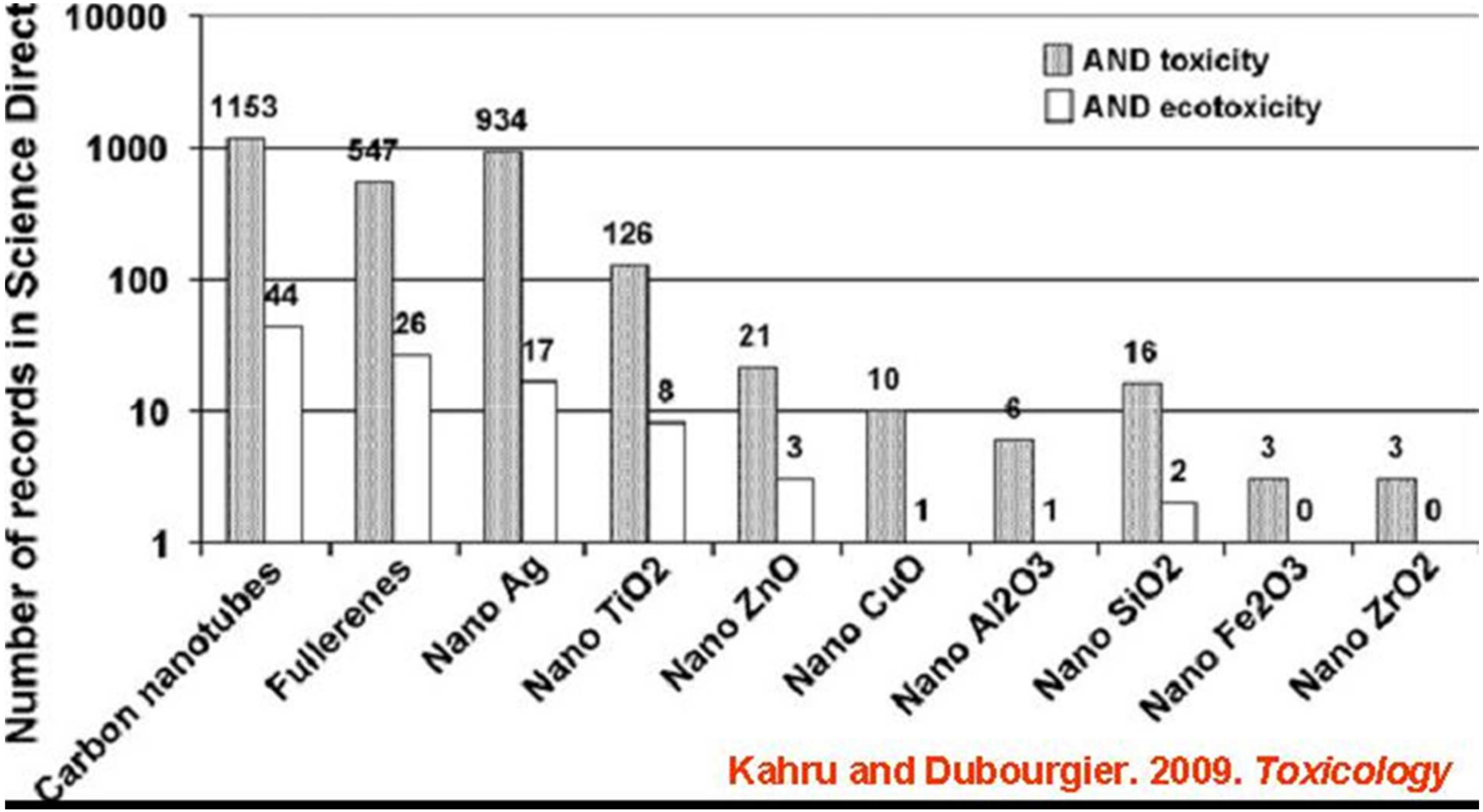

PAPER
PLASTIC
CANS

DATA SPREAD


Brar et al. 2010. Waste Management 30: 504-520
No. of publications
3500
3000
2500
2000
1500
1000
500
0
79.3 %
14.8 %
0.6 %
4.9 %
0.4 %
Synthesis
Air
Wastewater
Toxicity
Environmental Remediation
Wastewater sludge
Biosolids
Fields of publication


Haynes. 2010. Anal. Bioanal. Chem. 398
# of Nanotoxicology Papers Published
1400
1200
1000
800
600
400
200
0
Year

DATA SPREAD


Number of records in Science Direct
10000
1000
100
10
1
AND toxicity
AND ecotoxicity
1153
44
547
26
934
17
126
8
21
3
10
1
6
1
16
2
3
0
3
0
Carbon nanotubes
Fullerenes
Nano Ag
Nano TiO2
Nano ZnO
Nano CuO
Nano Al2O3
Nano SiO2
Nano Fe2O3
Nano ZrO2
Kahru and Dubourgier. 2009. Toxicology

SOME FUNDAMENTAL COMPLEXITIES

- Interaction with biological matter?
- Uptake routes: Do NM parameters influence uptake, how?
- Basis for biological response? Molecular definition
- Inducive level of dosage: environmentally relevant?
- Biomarkers of exposure: nano vs bulk

OLD SCIENCE SOLUTIONS FOR NEW TECHNOLOGY PROBLEMS

OVERALL APPROACH

THE OXIDATIVE STRESS HYPOTHESIS

1.

H_2O_2

O_2^- NO_3

$^{\cdot}OH$

NO $ONOO^-$

$ROO^{\cdot}$

2.

$2\,O_2^{\cdot -} + 2\,H^+ \xrightarrow{\text{superoxide dismutase}} H_2O_2 + O_2$

$H_2O_2 + 2\,GSH \longrightarrow 2\,H_2O + GSSG$

$2\,OH^- + 2\,GSH \longrightarrow H_2O + GSSG$

3.

Oxidative damage

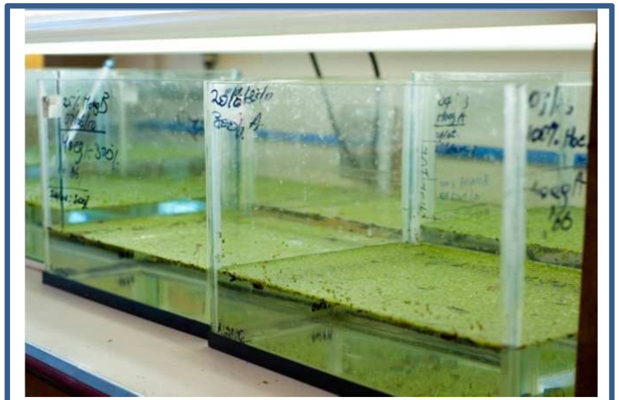
4.

Physiological alteration

LABORATORY MAINTANANCE and TESTING

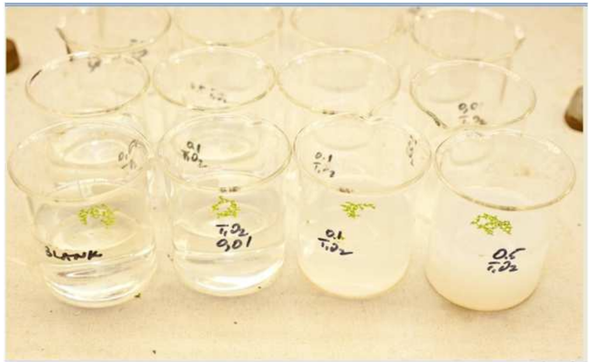
Free floating higher aquatic plant,

- easy laboratory maintenance,
- higher protein content,
- rapid growth.



Holding conditions:

- $22^{o}C \pm 2$
- cool-white fluorescent
- light:dark/8:16hrs
- weekly water renewal.



- Exposure period:

4 days-static and 14 days- static renewal

- Hoagland's Medium
- 5 replicates- 30 plants/replicate

Free radical activity

- ROS/RNS
- H_2O_2, $ROO^{\cdot}$, NO, $ONOO^{-}$
- DCFH-DiOxyQ probe

Enzymatic scavengers

- Catalase
- Superoxide dismutase
- Total antioxidant capacity

Size	Morphology	Surface area
• TEM	• TEM	• BET
• DLS	• XRD	

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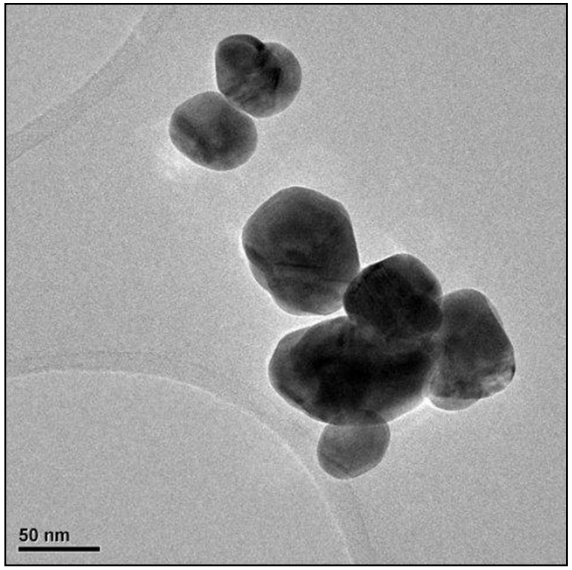
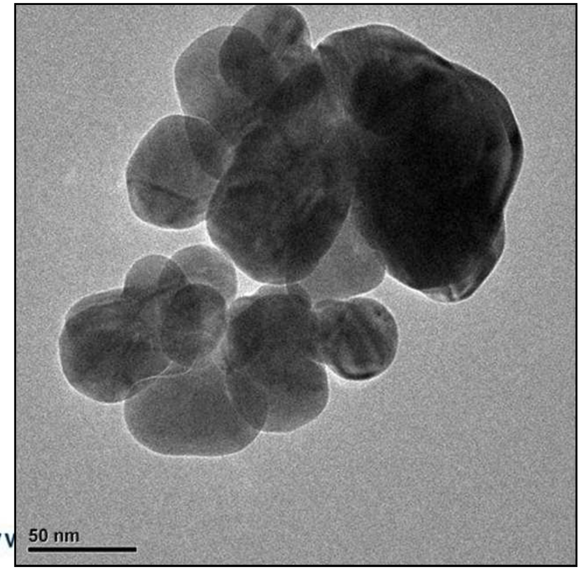
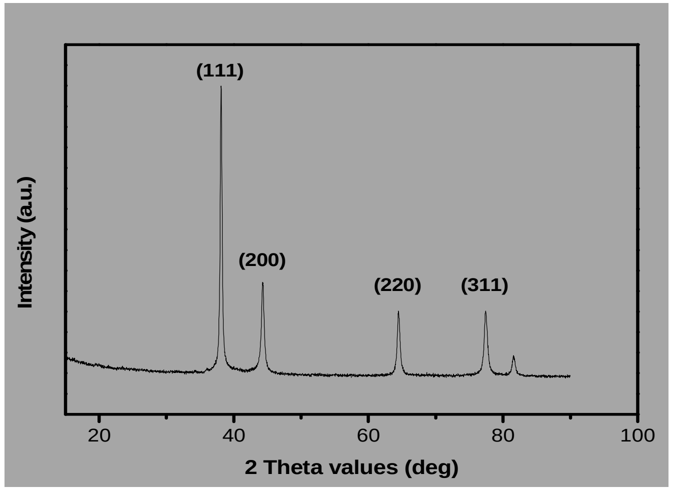
Ag nanoparticles





Sample	SA_{BET} (m^2/g)	Pore Volume (cm^3/g)	Particle size (nm)	Z-potential (mV)
nAg	3.399	0.01509	40-60	-16.3



Morphology
- Spherical nanoparticles.

Surface area
- Small relative to size.

XRD pattern
- Few crystal particles also detected.
- Pure phase: no impurities peaks detected.

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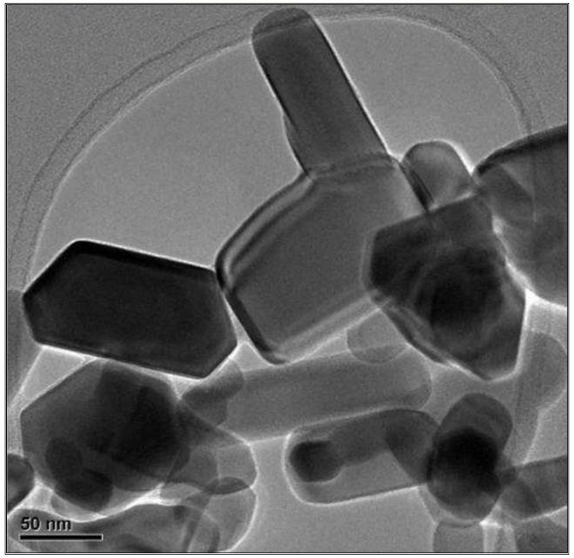
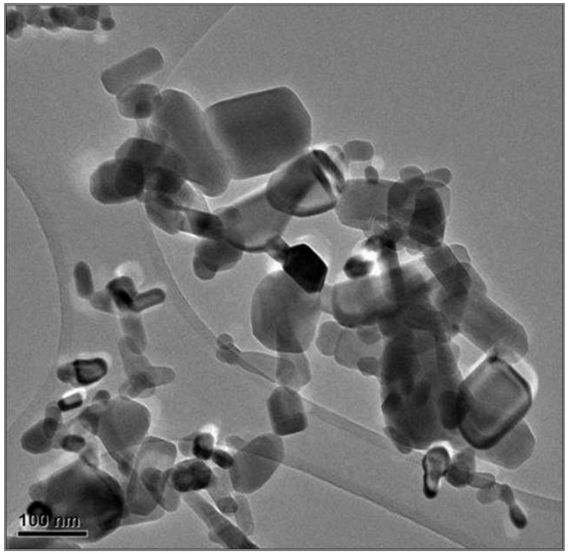
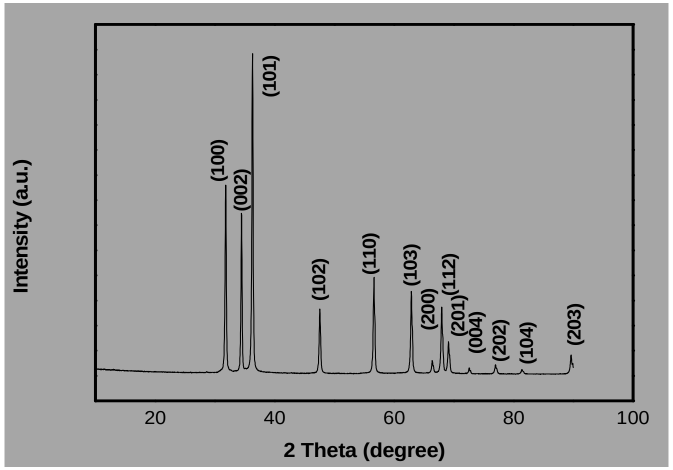
ZnO nanoparticles





Sample	SA_{BET} (m^2/g)	Pore Volume (cm^3/g)	Particle size (nm)	Z-potential (mV)
nZnO	11.44	0.03020	10-130	22.7
nAg	3.399	0.01509	40-60	-16.3



Morphology

- regular (20-50 nm) and irregular spheres (80-120 nm), rods (15-45 nm), cubes (10-130 nm) and hexagonal platelets (60-80 nm).

Surface area

- Higher than nAg although bigger sized.

XRD pattern

- High crystallisation: hexagonal crystal system.
- Pure phase: no impurities peaks detected.

Hydrodynamic size and surface charge potential

		Hydrodynamic size (nm)				Zeta potential (mV)			
Concentration (mg/L)		0.01	0.1	1	1000	0.01	0.1	1	1000
Test start	*n*ZnO	326.5	822	1020	1299	-9.9	-7.7	-8.8	-5.1
	*n*Ag	667	716	639	1313	-9.2	-6.8	-8.4	-3.6
4 days-test end	*n*ZnO	422	726	1158	1350	-9.6	-11	-10.7	-6.4
	*n*Ag	402	900	1300	727	-7.5	-10.1	-11.6	-5.6
14 days-test end	*n*ZnO	574.6	531	426	1129	-9.3	-10.3	-8.9	-4.9
	*n*Ag	760.95	352	629	365	-9.6	-9.3	-8.8	-5.1

Dissolved ionic species

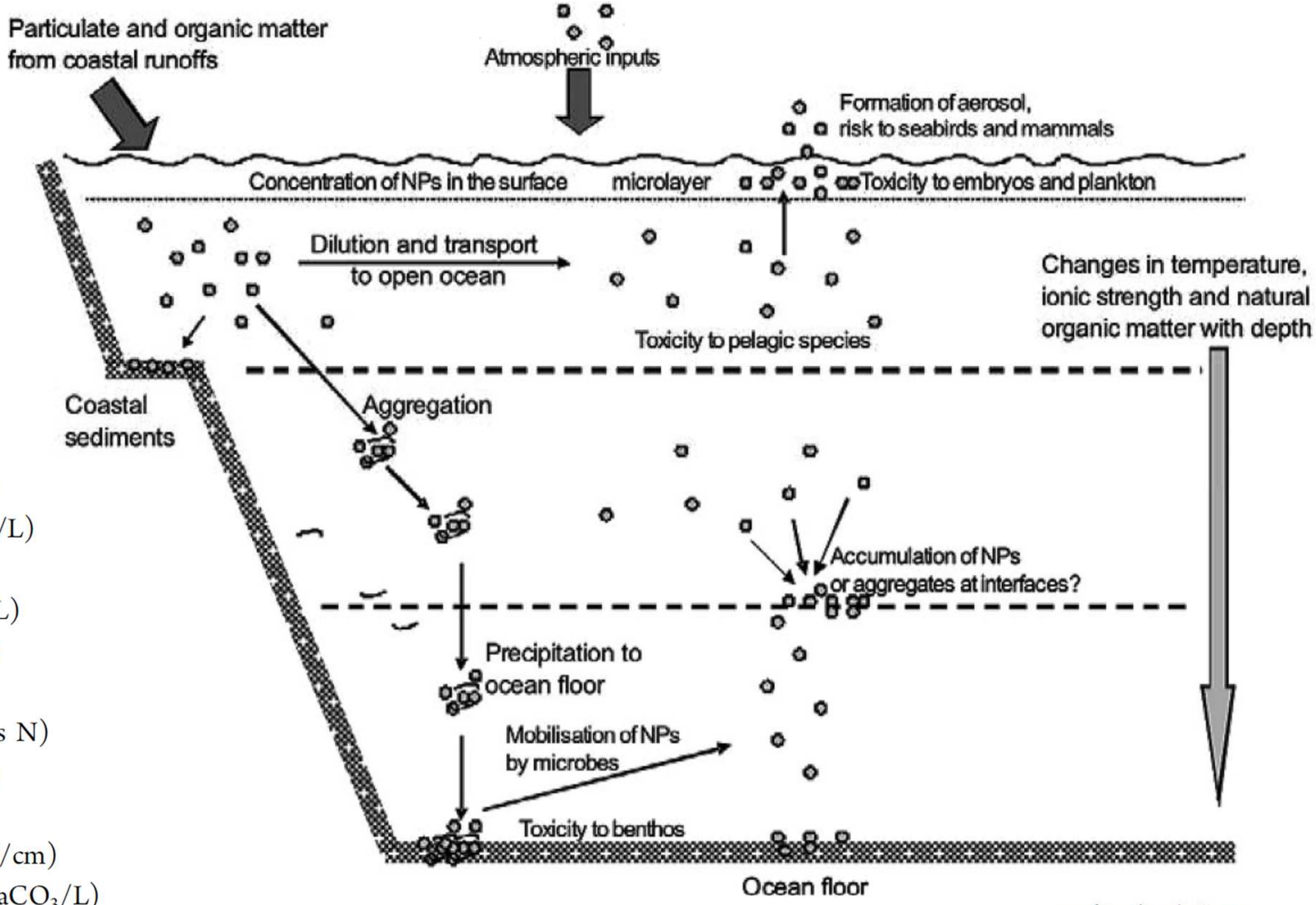
ENPs	Duration (days)	0.01 (mg/L)	0.1 (mg/L)	1 (mg/L)	1000 (mg/L)
Ag	4	<0.025	<0.025	<0.025	0.145
	14	<0.025	<0.025	<0.025	ND
ZnO	4	<0.025	<0.025	0.250	12
	14	<0.025	<0.025	0.025	13

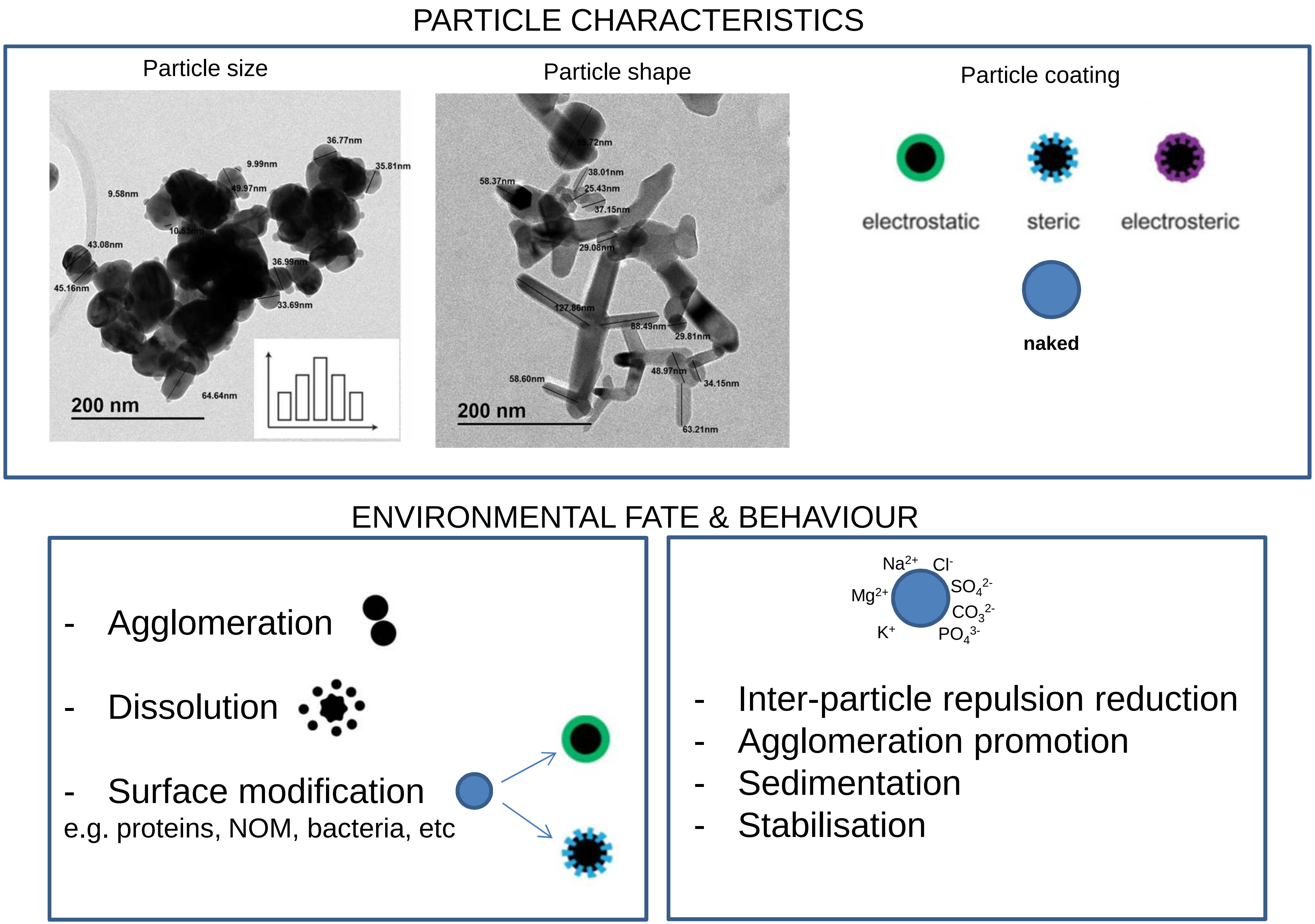
Overall

- Size change- particle growth by agglomeration.
- Reduction of particle surface charge, time influence.
- Generation of detectable ionic species, more so for nZnO

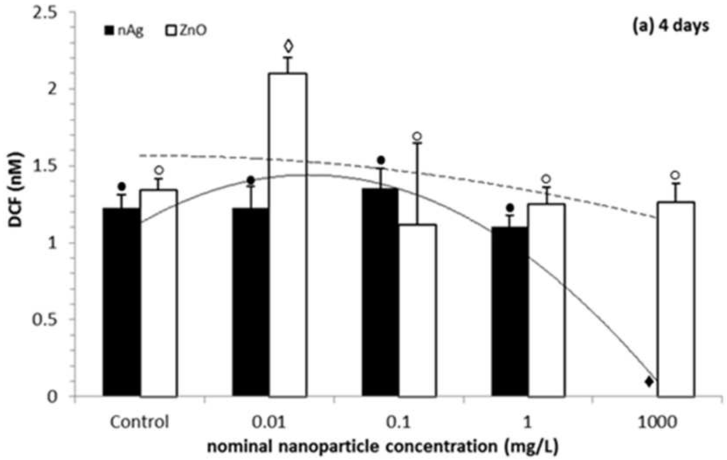
River constituents that can alter ENP stability

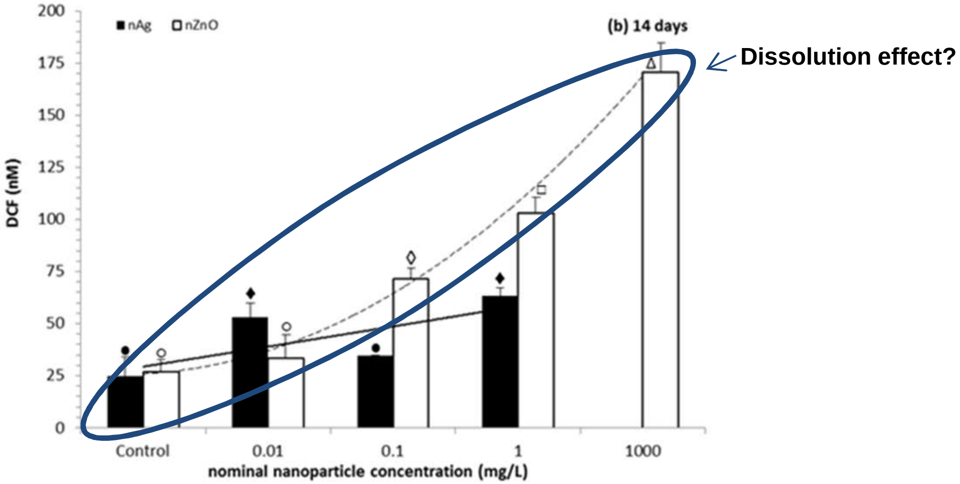
- calcium (mg/L)
- magnesium (mg/L)
- sodium (mg/L)
- potassium (mg/L)
- chloride (mg/L)
- sulfate (mg/L)
- nitrate (mg/L, as N)
- TOC (mg C/L)
- pH
- conductivity (μS/cm)
- alkalinity (mg $CaCO_3$/L)

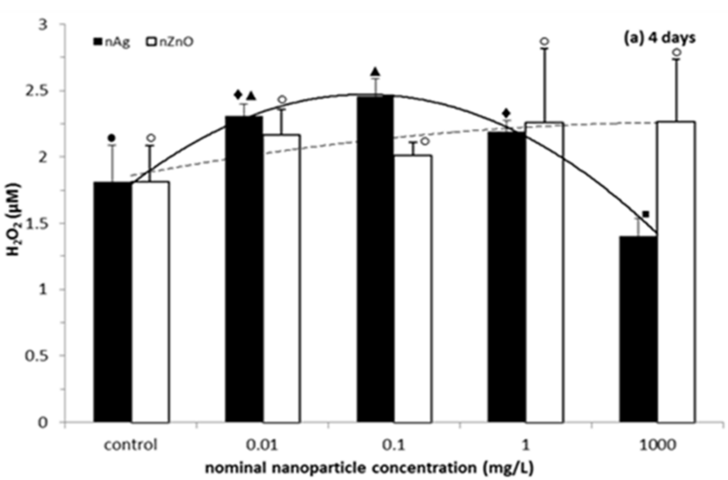


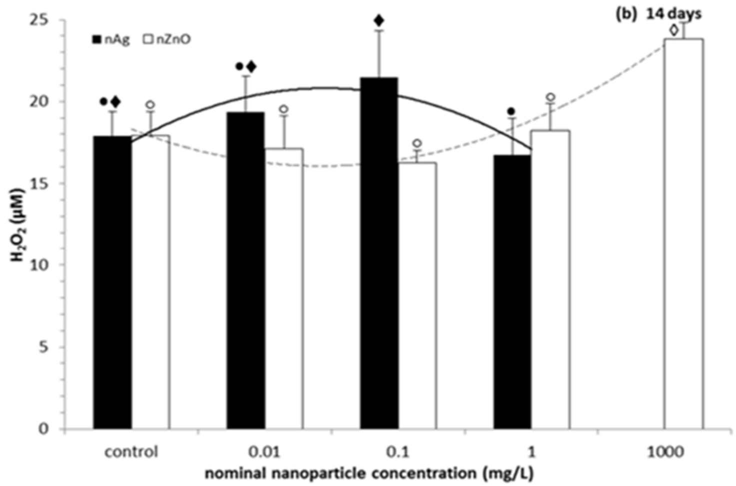

PARTICLE CHARACTERISTICS
Particle size
200 nm
Particle shape
200 nm
Particle coating
electrostatic
steric
electrosteric
naked
ENVIRONMENTAL FATE & BEHAVIOUR
- Agglomeration
- Dissolution
- Surface modification
e.g. proteins, NOM, bacteria, etc
Na2+
Cl-
Mg2+
SO42-
CO32-
K+
PO43-
- Inter-particle repulsion reduction
- Agglomeration promotion
- Sedimentation
- Stabilisation

FREE RADICALS: ROS/RNS and H_2O_2

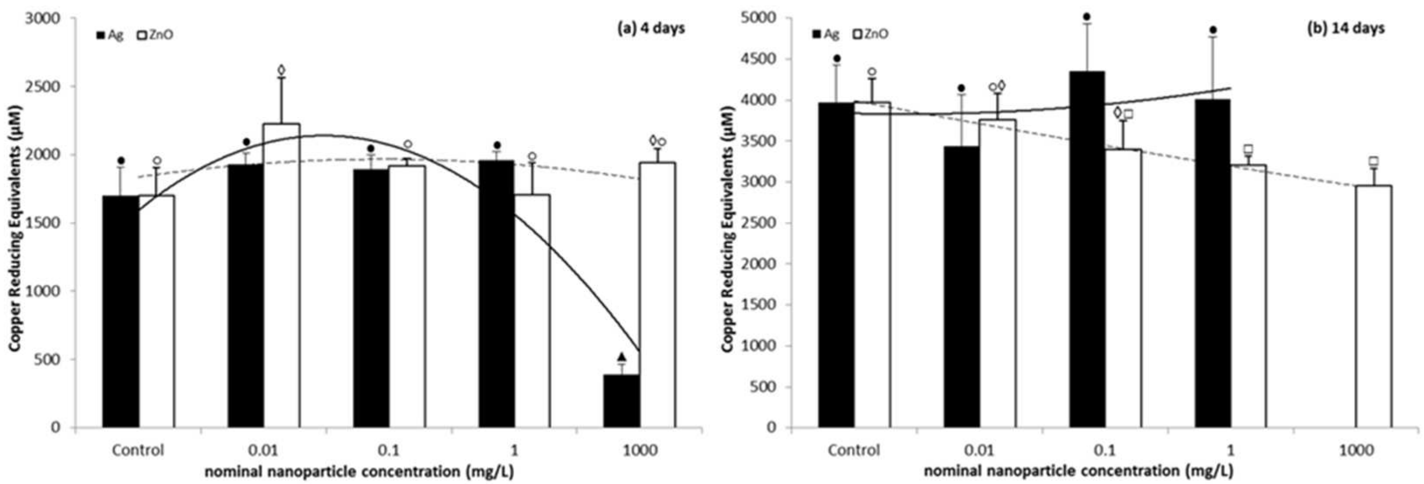


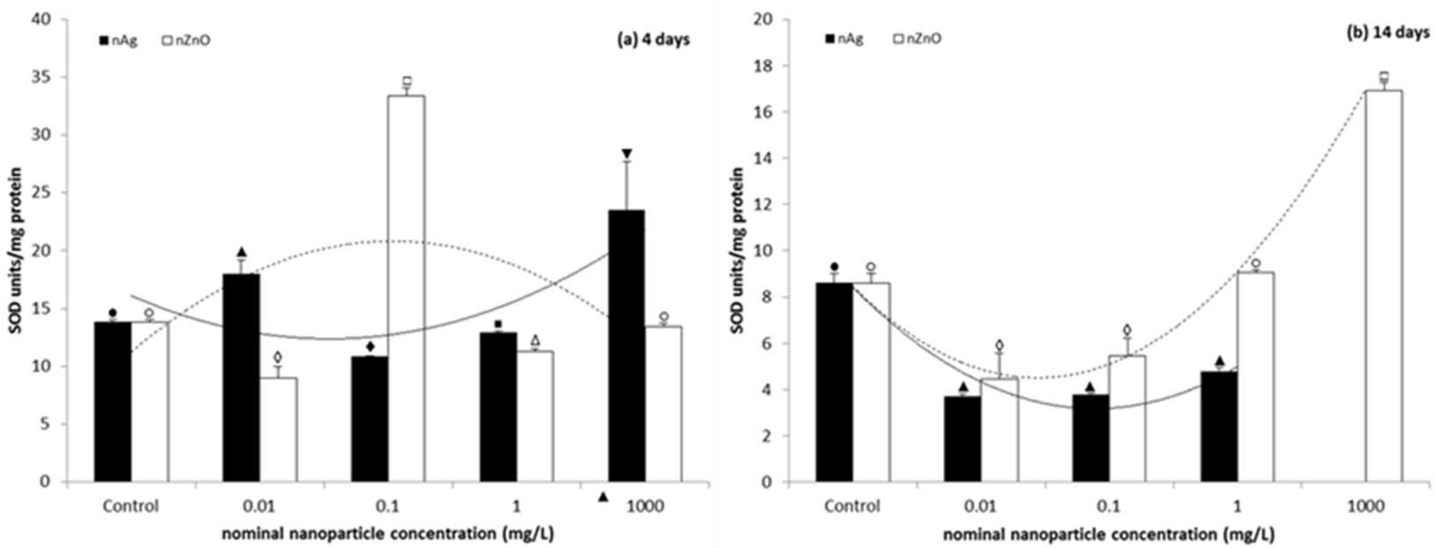






Total antioxidant capacity & Superoxide dismutase activity





CONCLUSIONS and THE FUTURE

- As received and in-test characterisation a basic necessity.
- Toxicity of metallic ENPs can be as a result of both particulates and ions- environmental conditions play a major role.
- “umbrella” assumptions are flawed for ENPs hazard evaluation.
- Prolonged persistence poses future effects- ENPs move in and out of solution.
- Successful in providing oxidative stress induction on a tiered approach.

FUTURE

- Detailed investigation of dissolution and agglomeration dynamics- size, shape and environmental conditions- mainly ionic strength. Masters study
- How the above translate into uptake and toxicity towards higher aquatic plants.

Environmental Science
Processes & Impacts

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PAPER

The oxidative toxicity of Ag and ZnO nanoparticles towards the aquatic plant *Spirodela punctuta* and the role of testing media parameters

Cite this: DOI: 10.1039/c3em00235g

Melusi Thwala,[ab] Ndeke Musee,*[ac] Lucky Sikhwivhilu[d] and Victor Wepener[b]

The toxicity effects of silver (nAg) and zinc oxide (nZnO) engineered nanoparticles (ENPs) on the duckweed *Spirodela punctuta* were studied to investigate the potential risks posed by these ENPs towards higher aquatic plants. The influence of media abiotic factors on the stability of the ENPs was also evaluated. Marked agglomeration of ENPs was observed after introduction into testing media whereby large particles settled out of suspension and accumulated at the bottom of testing vessels. The high ionic strength (IS) promoted agglomeration of ENPs because it reduced the inter-particle repulsion caused by a reduction in their surface charge. Low dissolution was observed for nAg, reaching only 0.015% at 1000 mg L^{-1}, whilst improved dissolution was observed for nZnO, only falling below analytical quantification at 0.1 mg L^{-1} and lower. The quantification of free radicals namely, reactive oxygen and nitrogen species (ROS/RNS) and hydrogen peroxide (H_2O_2), indicated the induction of oxidative stress in plants exposed to the ENPs. A definite dose influence was observed for ROS/RNS volumes in plants exposed to nZnO for 14 days, a response not always observed. The total antioxidant capacity (TAC) and superoxide dismutase (SOD) activity in plants indicated varying degrees of oxidative toxicity caused by exposure to ENPs. This toxicity was driven mainly by particulates in plants exposed to nAg, whilst dissolved Zn^{2+} was the main driver for toxicity in plants exposed to nZnO. Our findings suggest that the toxicity of nAg and nZnO could be caused by both the particulates and ionic forms, as modified by media properties.

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rsc.li/process-impacts

Environmental impact

The environmental impacts of metallic engineered nanoparticles are still yet to be well elucidated. Current literature strongly suggests an elevated toxic potential at the nanoscale relative to bulk counterparts; however, the basis of such toxicity still remains unclear. Additionally, the influence of environmental abiotic factors on the chemical and physical stability of nanoparticles is often not investigated, therefore there is little understanding of how this translates to the toxicity potential. At present there is limited knowledge about their toxicity potential towards higher aquatic plants. This study aims to better understand the influence of environmental factors on the stability of metallic nanoparticles, and, contribute towards data generation on their toxic potential towards aquatic plants.

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