University of the Aegean
Department of Environment

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Toxicity of engineered nanoparticles in aquatic organisms

University of the Aegean

- Situated in the Aegean Archipelago, the University of the Aegean (established in 1984) is a state, multi-campus University with more than 12.000 students, dispersed over six Aegean islands: Lesvos, Chios, Samos, Rhodes, Syros and Lemnos

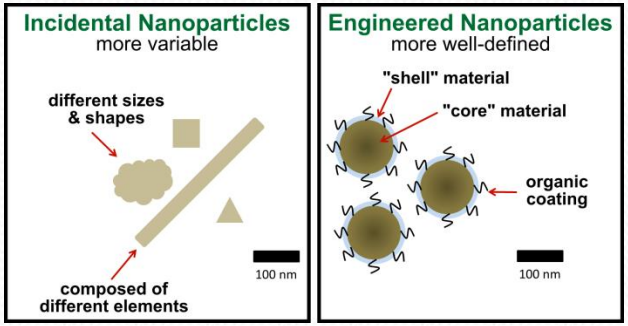
- Department of Environment research areas: environmental chemistry, air pollution, wastewater treatment, ecotoxicology, environmental policy & environmental management

ENPs

- Engineered nanoparticles (ENPs) are man-made particles having diameters from 1-100nm with unique properties compared to their bulk counterparts => applications in > 1300 consumer products

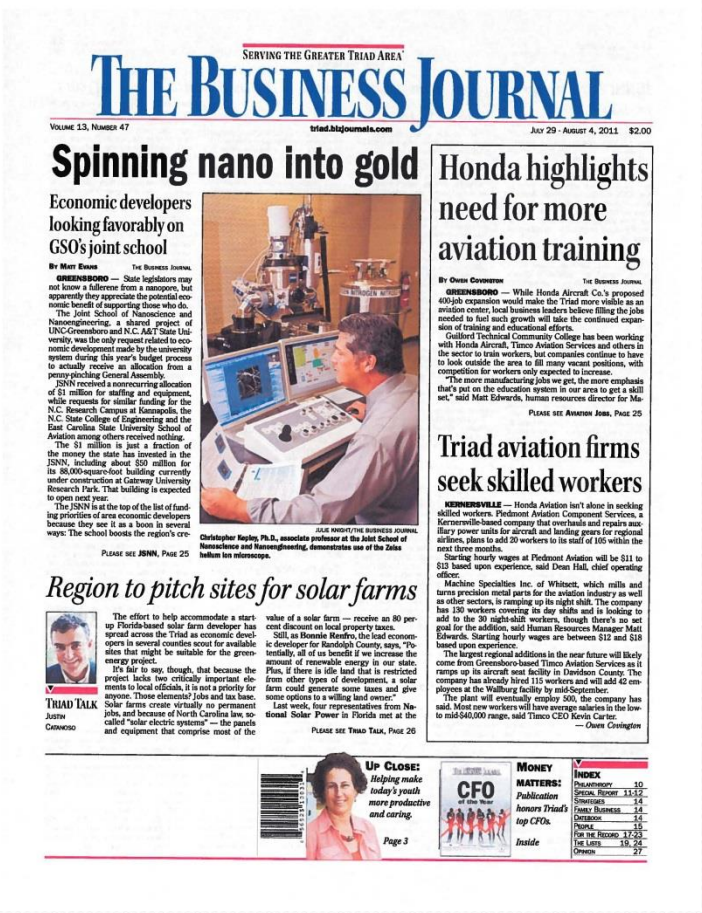
- High surface to volume ratio => increased reactivity and toxicity

- Altered properties compared to bulk materials (size, shape, composition)



- High volume production chemicals (lack of reliable data estimates)

In the news



SERVING THE GREATER TRIAD AREA

THE BUSINESS JOURNAL

VOLUME 13, NUMBER 47 — triad.bizjournals.com — JULY 29 - AUGUST 4, 2011 — $2.00

Spinning nano into gold

Economic developers looking favorably on GSO's joint school

BY MATT EVANS — THE BUSINESS JOURNAL

GREENSBORO — State legislators may not know a fullerene from a nanopore, but apparently they appreciate the potential economic benefit of supporting those who do.

The Joint School of Nanoscience and Nanoengineering, a shared project of UNC-Greensboro and N.C. A&T State University, was the only request related to economic development made by the university system during this year's budget process to actually receive an allocation from a penny-pinching General Assembly.

JSNN received a nonrecurring allocation of $1 million for staffing and equipment, while requests for similar funding for the N.C. Research Campus at Kannapolis, the N.C. State College of Engineering and the East Carolina State University School of Aviation among others received nothing.

The $1 million is just a fraction of the money the state has invested in the JSNN, including about $50 million for its 88,000-square-foot building currently under construction at Gateway University Research Park. That building is expected to open next year.

The JSNN is at the top of the list of funding priorities of area economic developers because they see it as a boon in several ways: The school boosts the region's cre-

PLEASE SEE JSNN, PAGE 25

JULIE KNIGHT/THE BUSINESS JOURNAL

Christopher Ropley, Ph.D., associate professor at the Joint School of Nanoscience and Nanoengineering, demonstrates use of the Zeiss helium ion microscope.

Honda highlights need for more aviation training

BY OWEN COVINGTON — THE BUSINESS JOURNAL

GREENSBORO — While Honda Aircraft Co.'s proposed 400-job expansion would make the Triad more visible as an aviation center, local business leaders believe filling the jobs needed to fuel such growth will take the continued expansion of training and educational efforts.

Guilford Technical Community College has been working with Honda Aircraft, Timco Aviation Services and others in the sector to train workers, but companies continue to have to look outside the area to fill many vacant positions, with competition for workers only expected to increase.

"The more manufacturing jobs we get, the more emphasis that's put on the education system in our area to get a skill set," said Matt Edwards, human resources director for Ma-

PLEASE SEE AVIATION JOBS, PAGE 25

Triad aviation firms seek skilled workers

KERNERSVILLE — Honda Aviation isn't alone in seeking skilled workers. Piedmont Aviation Component Services, a Kernersville-based company that overhauls and repairs auxiliary power units for aircraft and landing gears for regional airlines, plans to add 20 workers to its staff of 105 within the next three months.

Starting hourly wages at Piedmont Aviation will be $11 to $13 based upon experience, said Dean Hall, chief operating officer.

Machine Specialties Inc. of Whitsett, which mills and turns precision metal parts for the aviation industry as well as other sectors, is ramping up its night shift. The company has 130 workers covering its day shifts and is looking to add to the 30 night-shift workers, though there's no set goal for the addition, said Human Resources Manager Matt Edwards. Starting hourly wages are between $12 and $18 based upon experience.

The largest regional additions in the near future will likely come from Greensboro-based Timco Aviation Services as it ramps up its aircraft seat facility in Davidson County. The company has already hired 115 workers and will add 42 employees at the Wallburg facility by mid-September.

The plant will eventually employ 500, the company has said. Most new workers will have average salaries in the low- to mid-$40,000 range, said Timco CEO Kevin Carter.

— *Owen Covington*

Region to pitch sites for solar farms

TRIAD TALK — JUSTIN CARMONOSO

The effort to help accommodate a start-up Florida-based solar farm developer has spread across the Triad as economic developers in several counties scout for available sites that might be suitable for the green-energy project.

It's fair to say, though, that because the project lacks two critically important elements to local officials, it is not a priority for anyone. Those elements? Jobs and tax base. Solar farms create virtually no permanent jobs, and because of North Carolina law, so-called "solar electric systems" — the panels and equipment that comprise most of the value of a solar farm — receive an 80 percent discount on local property taxes.

Still, as Bonnie Renfro, the lead economic developer for Randolph County, says, "Potentially, all of us benefit if we increase the amount of renewable energy in our state. Plus, if there is idle land that is restricted from other types of development, a solar farm could generate some taxes and give some options to a willing land owner."

Last week, four representatives from National Solar Power in Florida met at the

PLEASE SEE TRIAD TALK, PAGE 26

UP CLOSE: *Helping make today's youth more productive and caring.* *Page 3*

CFO of the Year — *Inside*

MONEY MATTERS: *Publication honors Triad's top CFOs.*

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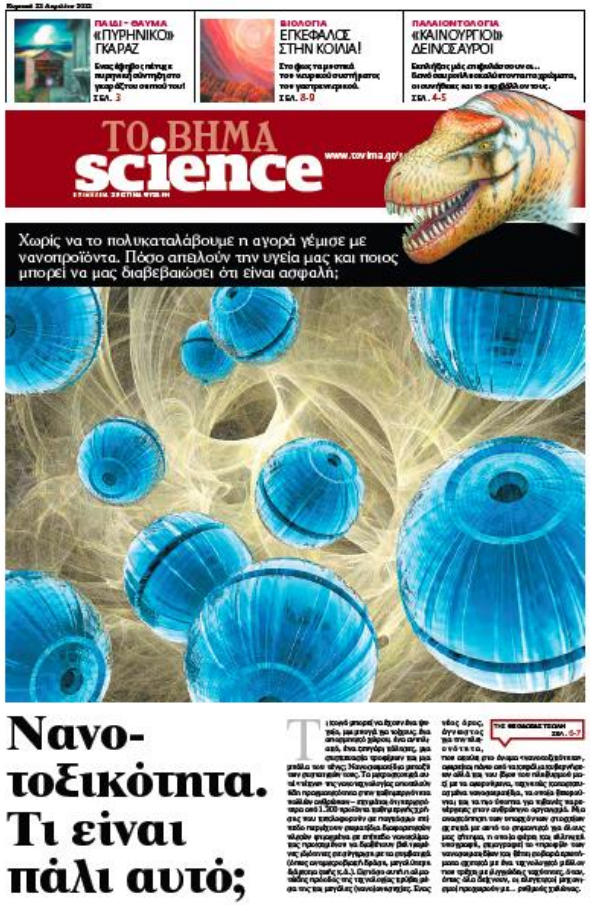

ΠΑΛΙ - ΘΑΥΜΑ «ΠΥΡΗΝΙΚΟ» ΓΚΑΡΑΖ — Σ.ΕΛ. 3

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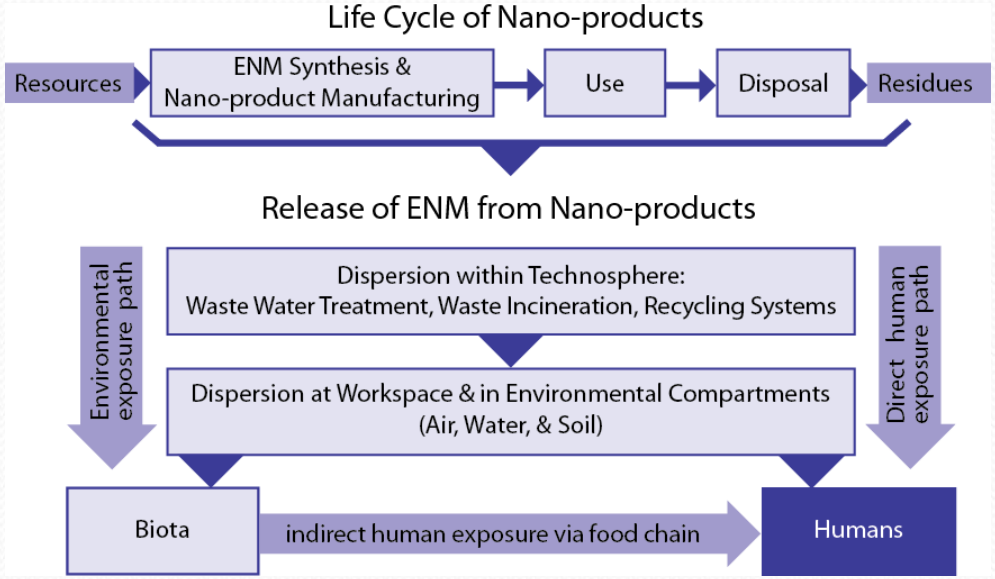
ΤΟ ΒΗΜΑ science — www.tovima.gr

Χωρίς να το πολυκαταλάβουμε η αγορά γέμισε με νανοπροϊόντα. Πόσο απειλούν την υγεία μας και ποιος μπορεί να μας διαβεβαιώσει ότι είναι ασφαλή;

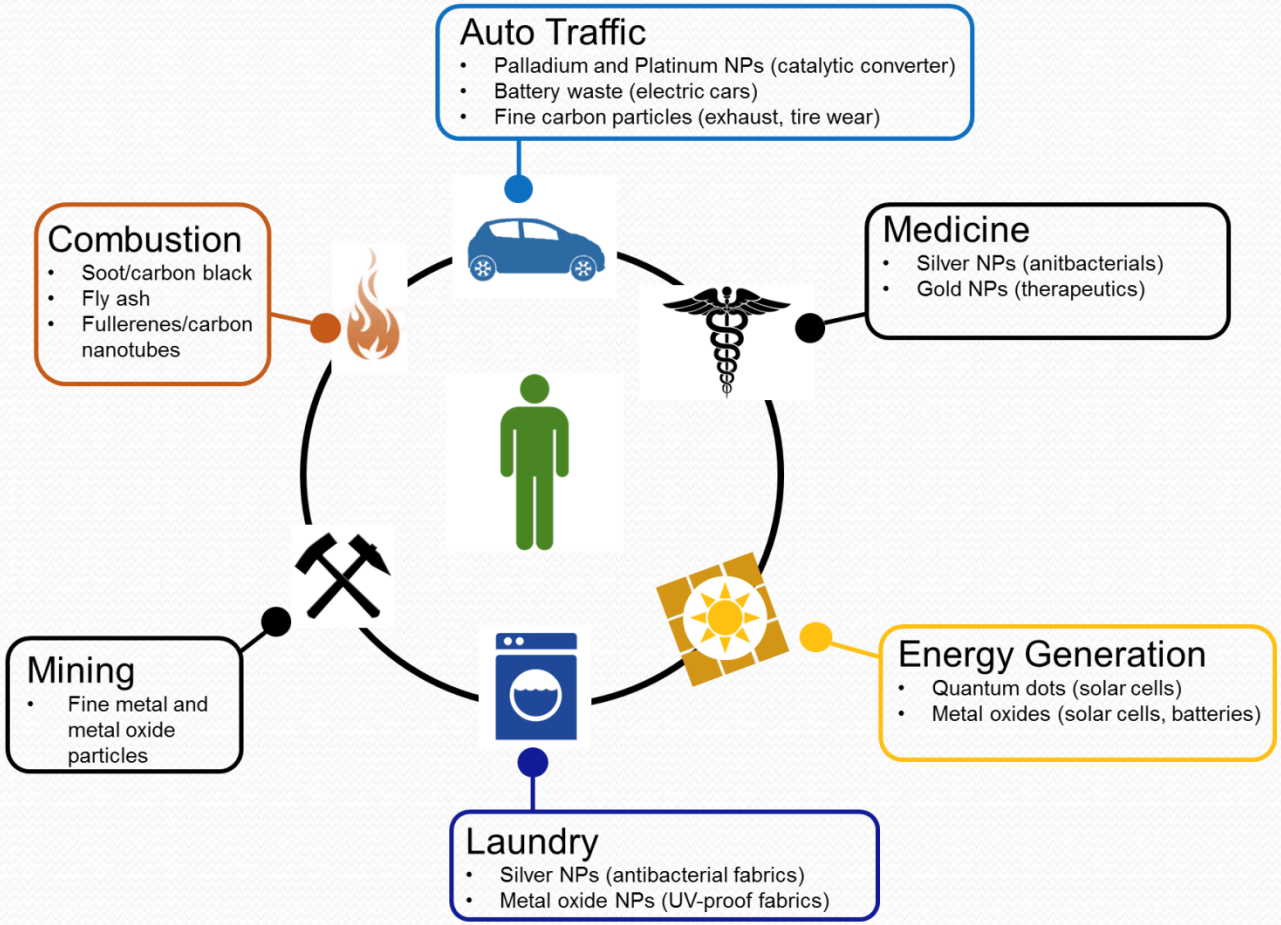
Νανο-τοξικότητα. Τι είναι πάλι αυτό;

Release into the environment

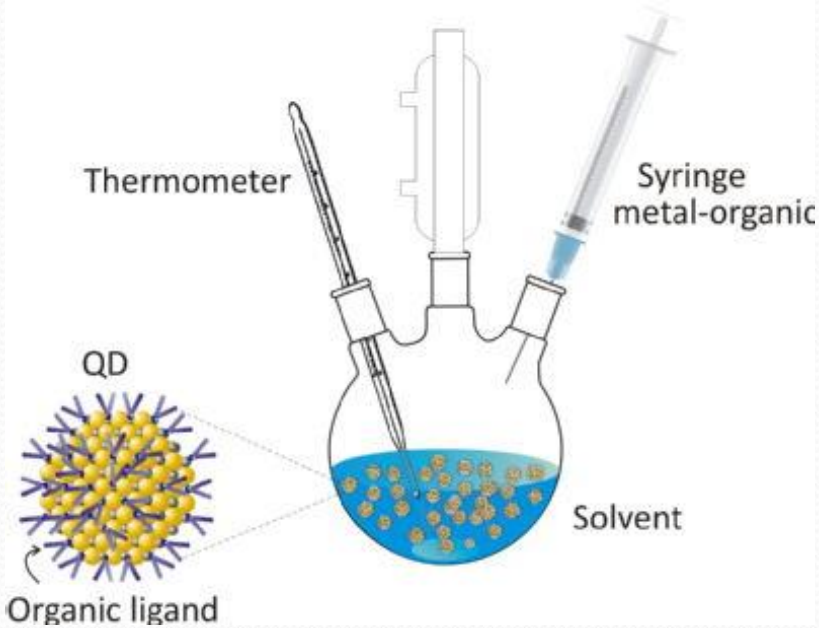
- Production and manufacturing processes
- Transportation leaks
- Intentional and unintentional ENP-containing product release
- Recycling emissions and product disposal



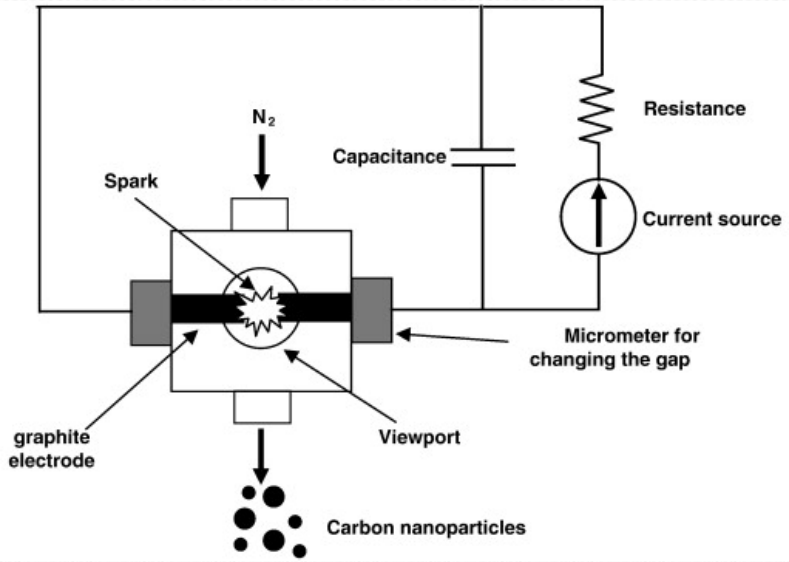
ENP uses and routes of human exposure

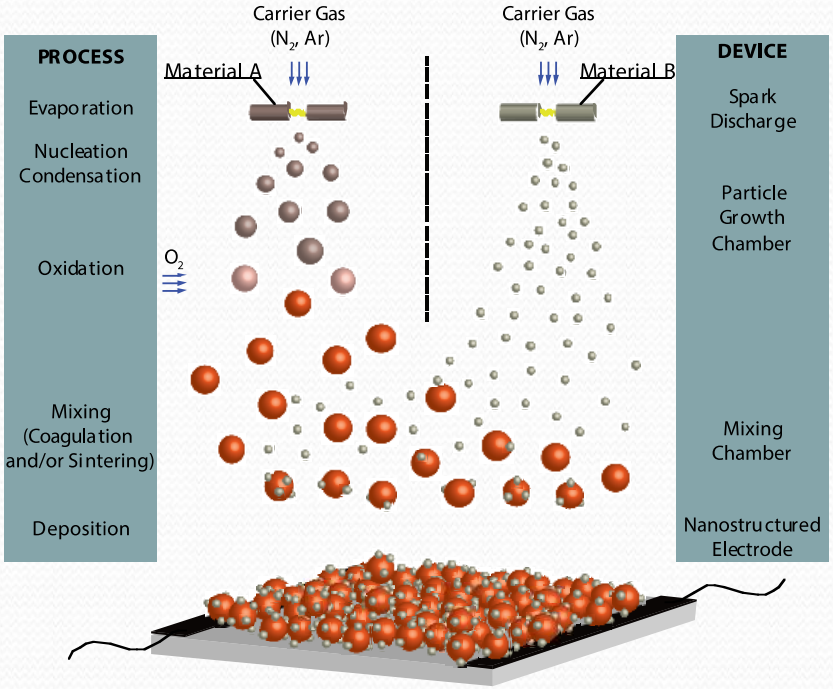


ENP synthesis – liquid phase



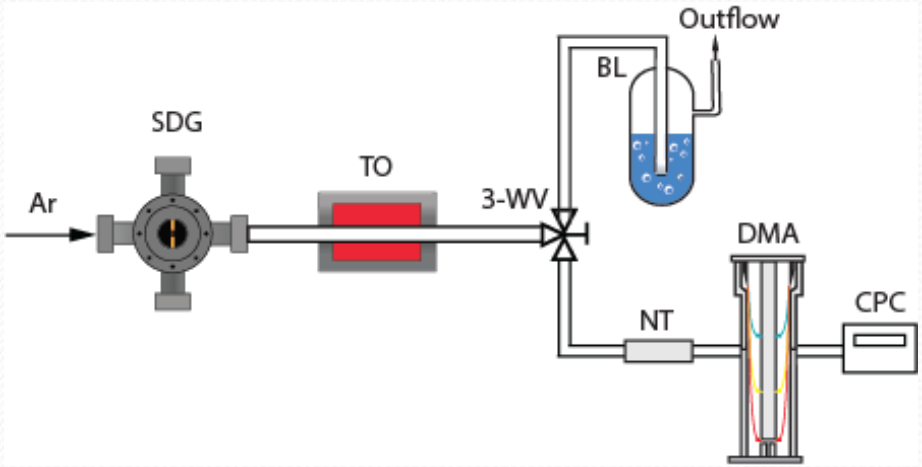
ENP synthesis – gas phase





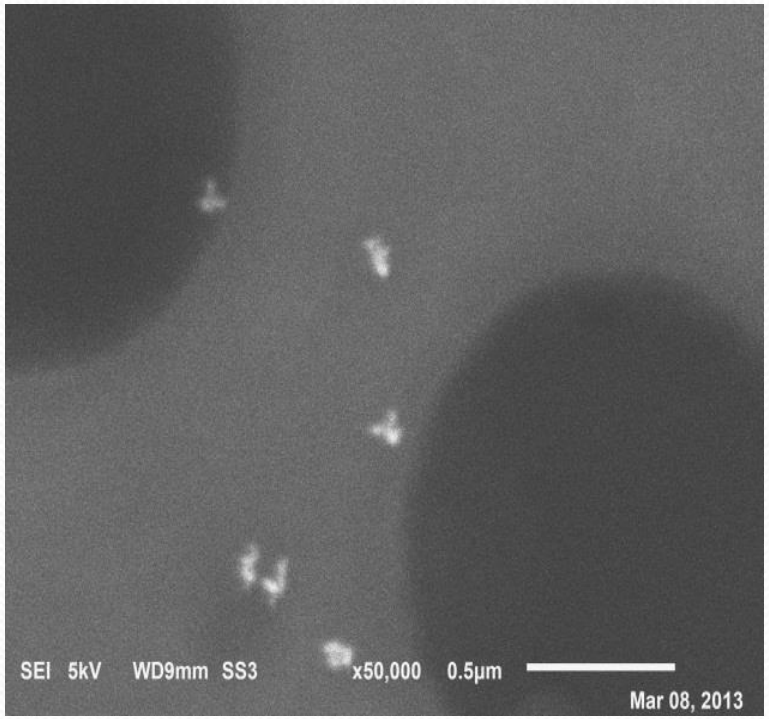
Spark ablation schematic layout

- SDG: spark discharge generator
- TO: tube oven
- 3WV: three-way valve
- BL: bubbler
- NT: aerosol neutralizer
- DMA: differential mobility analyzer
- CPC: condensation particle counter

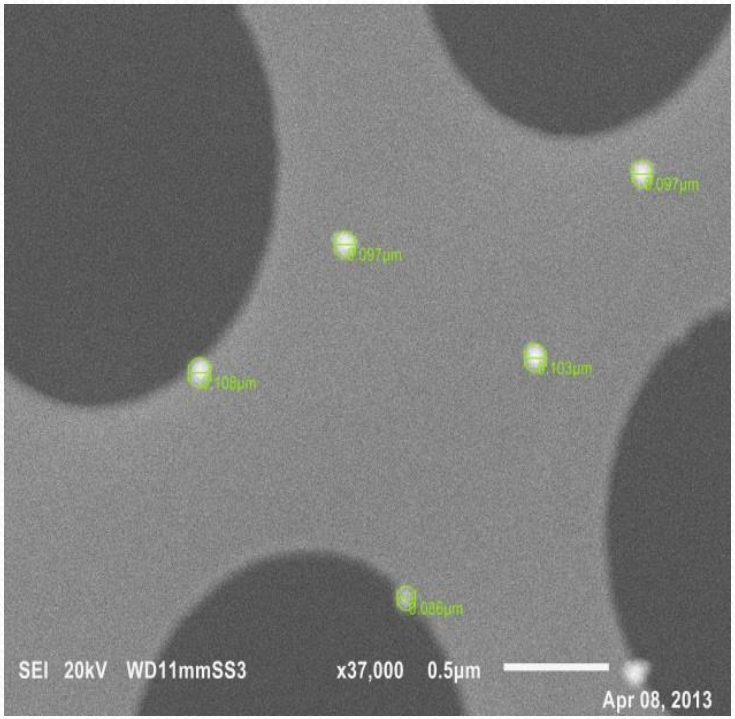


ENP shape and size

Oven Temp. 375 ° C



Oven Temp. 990 ° C



Toxicity of ENPs to aquatic organisms

- The aquatic environment is at risk of exposure to ENPs as it is a sink for most environmental contaminants
- Industrial waste and urban water sewage end up in aquatic systems (lakes, rivers, etc)
- More potential routes of uptake by aquatic organisms than terrestrial (ingestion, gill entry, cellular uptake, skin uptake)

- Nanotoxicity still at infant stage
- Large knowledge gaps for most aquatic organisms

- Total silver ion concentrations in aquatic environments around the world have been reported at levels ranging between 0.1 and 120 μg/L

Aims of the study

- Determine if high purity AgNPs and AuNPs produced by spark ablation having a diameter of 20-80 nm are toxic to the aquatic organism *L. Minor*

- Examine if purity affects the toxic behaviour of AgNPs to *L. minor* and compare our results with previous studies on AgNPs

Lemna minor

- Aquatic duckweed
- Rapidly growing
- Simplest and smallest floating plant on Earth
- Food for many aquatic fish and birds
- Model system in ecotoxicology and toxicity testing (OECD and US EPA protocols)

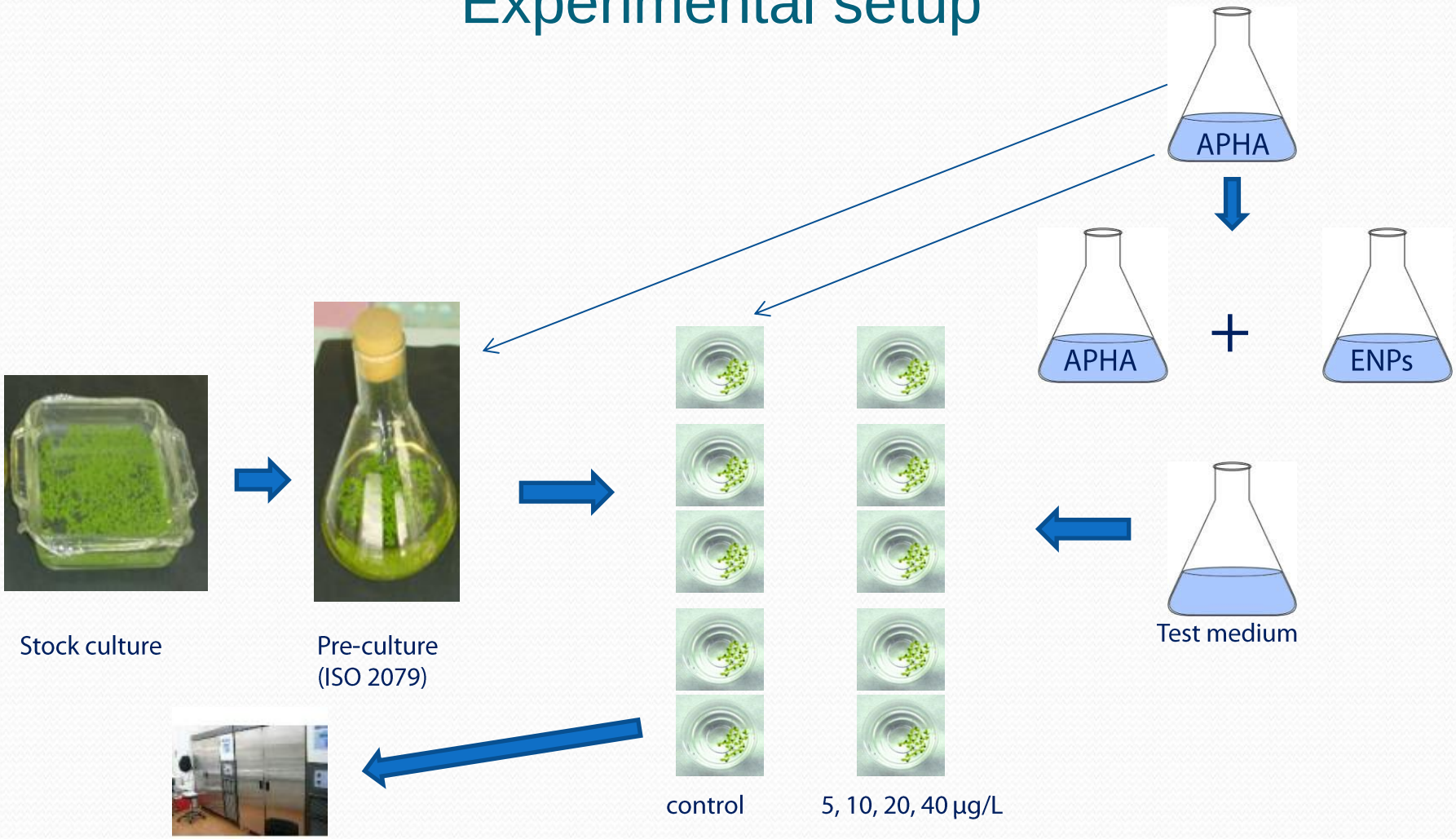
Silver NPs

- Antimicrobial properties
- Used in textiles, footwear, paints, wound dressings, cosmetics, medical plastics, conductive inks & biosensors
- Toxicity is mainly due to ionic form Ag+
- AgNPs have been previously shown to be toxic to *L. minor* (Gubbins *et al.* 2011, Üçüncü *et al.* 2014)

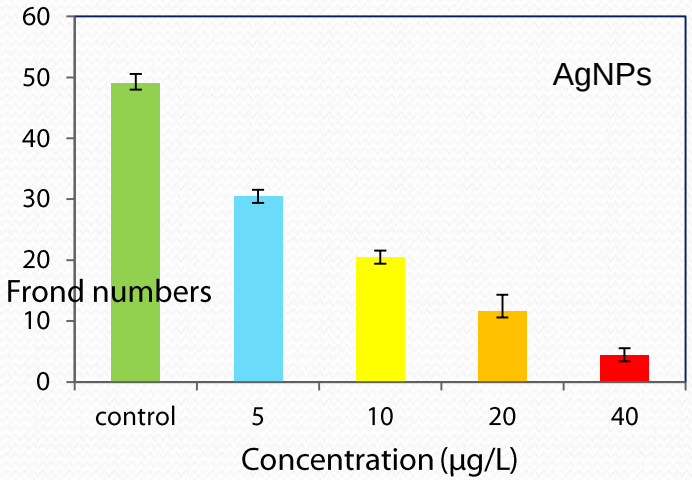
Gold NPs

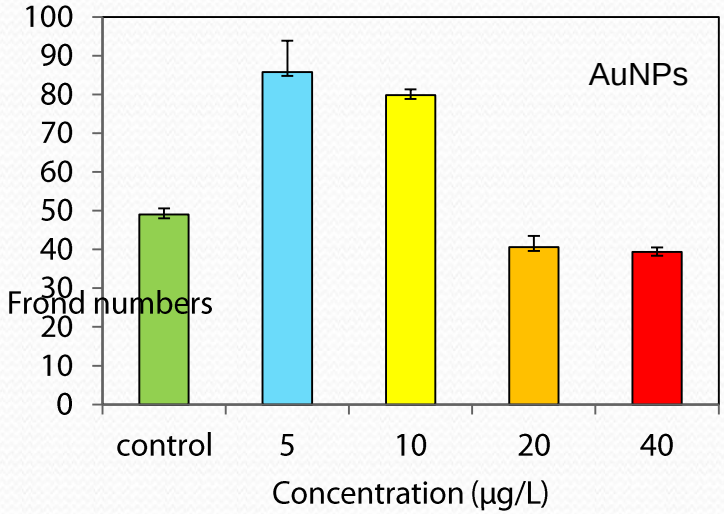
- Optical and electronic properties
- Used in organic photovoltaics, sensory probes, therapeutic agents, drug delivery, electronic conductors and catalysis
- No literature on AuNP exposure of *L. minor*. A recent study reported toxicity on the aquatic plant *Ceratophyllum demersum*

Experimental setup

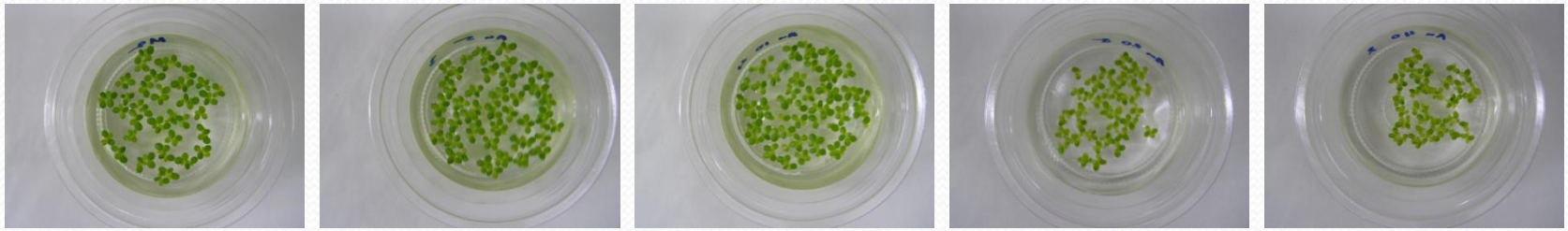


Results – frond numbers

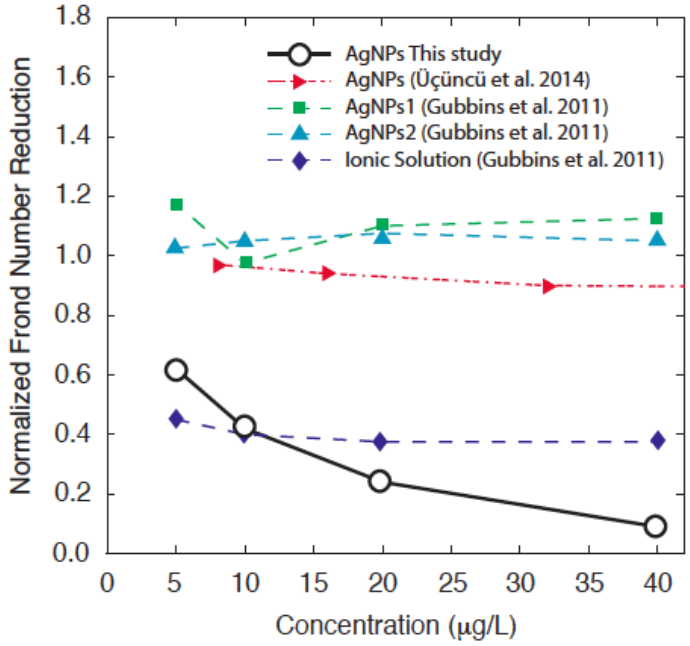




control | 5 μg/L AuNPs | 10 μg/L AuNPs | 20 μg/L AuNPs | 40 μg/L AuNPs

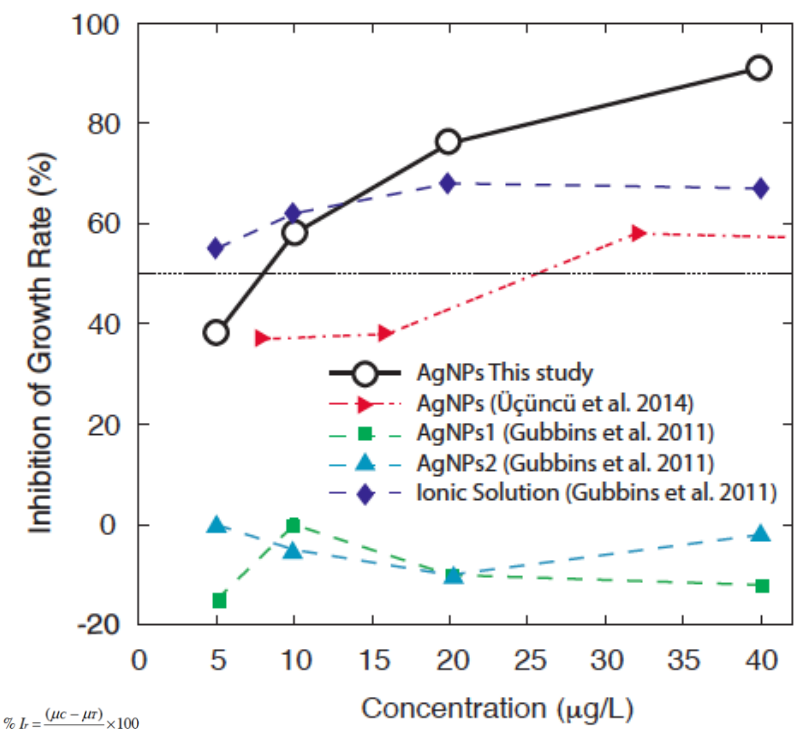


Results – frond number reduction



- Our study: AgNPs 20 - 80 nm (spark ablation)
- AgNPs1 7-30 nm, AgNP2 40-110 nm, ionic solution (liquid phase technique, Gubbins *et al.* 2011)
- AgNPs 5-20 nm (laser ablation, Üçüncü *et al*. 2014)

Results – inhibition of growth rate



$$\% I_r = \frac{(\mu c - \mu r)}{\mu c} \times 100$$

where:
- $\% I_r$: percent inhibition in average specific growth rate
- μ_C : mean value for μ in the control
- μ_T : mean value for μ in the treatment group

- Our study: AgNPs 20 - 80 nm (spark ablation)
- AgNPs 1 7-30 nm, AgNP 2 40-110 nm, ionic solution (liquid phase technique, Gubbins *et al.* 2011)
- AgNPs 5-20 nm (laser ablation, Üçüncü *et al*. 2014)

Conclusions

- AgNPs were toxic to *L.minor* even at the lowest tested concentration (5 μg/L)
- Frond number inhibition for AgNPs increased with increasing concentration
- In comparison to previous studies, our AgNP results are in agreement with the ionic silver solution and not the AgNP results of Gubbins *et al*. (2011), possibly due to higher impurities and capping agents
- Nanoparticle purity can affect a toxicity experiment result

- At lower concentrations (5 and 10 μg/L) AuNPs had a positive effect on frond number => hormesis?
- Not toxic to *L.minor* at concentrations of 20-40 μg/L

Future work

- Since ENPs produced by gas-phase methods are of the highest possible purity, it is recommended that these techniques are used to study nanoparticles toxicity
- Standardized protocols and study design for toxicity studies
- More research into the effects of NPs aquatic organisms is needed to provide a broader picture of the toxicity of these particles to different types of organisms
- Examine the effects of different capping agents on toxicity, as coatings are an important factor in the toxicity of Ag particles (due to silver ion release)

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- Dr. Vaya Kati @ Benakeio Phytopathological Institute (Greece)

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Thank you for your attention