СИБИРСКИЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ
SIBERIAN FEDERAL UNIVERSITY

III International Scientific Conference
BIOTECHNOLOGY OF NEW MATERIALS
- ENVIRONMENT - QUALITY OF LIFE 2018

STATE OF ART IN NANOCARRIERS AIMING AGRICULTURE AND ENVIRONMENTAL APPLICATIONS

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SÃO PAULO STATE UNIVERSITY
BRAZIL

2018

unesp

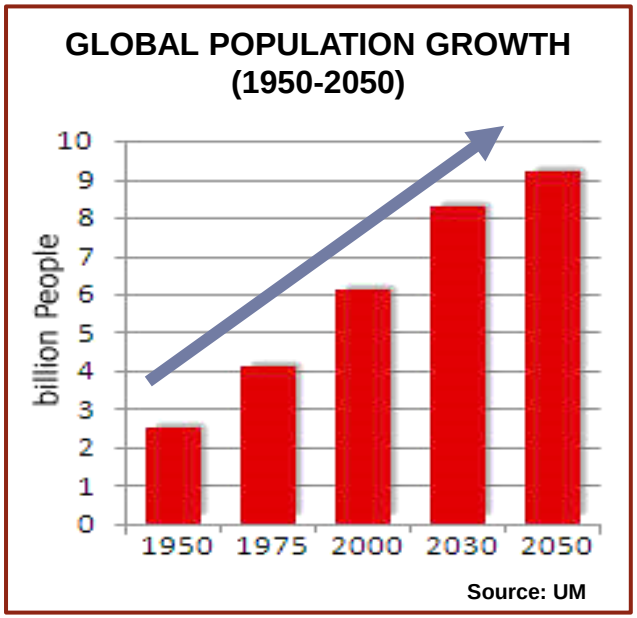
Outlines

ENVIRONMENTAL NANOTECHNOLOGY LAB

- Nanotechnology - trends
- Applications in Agriculture
- Examples
  - Herbicides
  - Botanical insecticides/acaricides
  - Botanical repellents
- Conclusions, gaps, obstacles

Population vs Food

Environmental Nanotechnology Lab



AGRICULTURAL DEVELOPMENT

SOIL AND WATER MANAGEMENT

BIOLOGICAL PEST CONTROL

ORGANIC FERTILIZERS

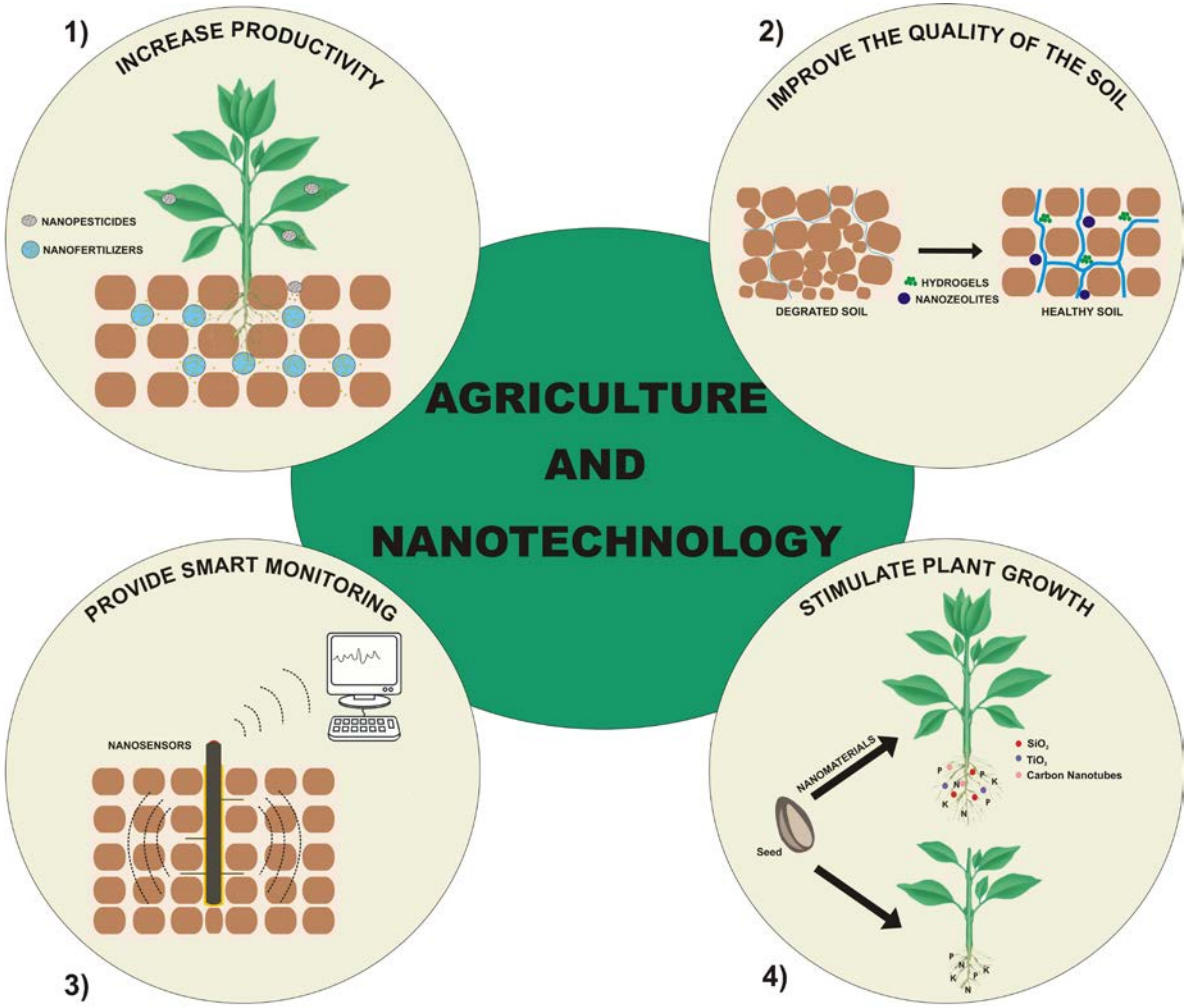
PESTICIDES

MECHANIZATION

INCREASED FOOD PRODUCTION

Nanotechnology: Current and future trends

ENVIRONMENTAL NANOTECHNOLOGY LAB



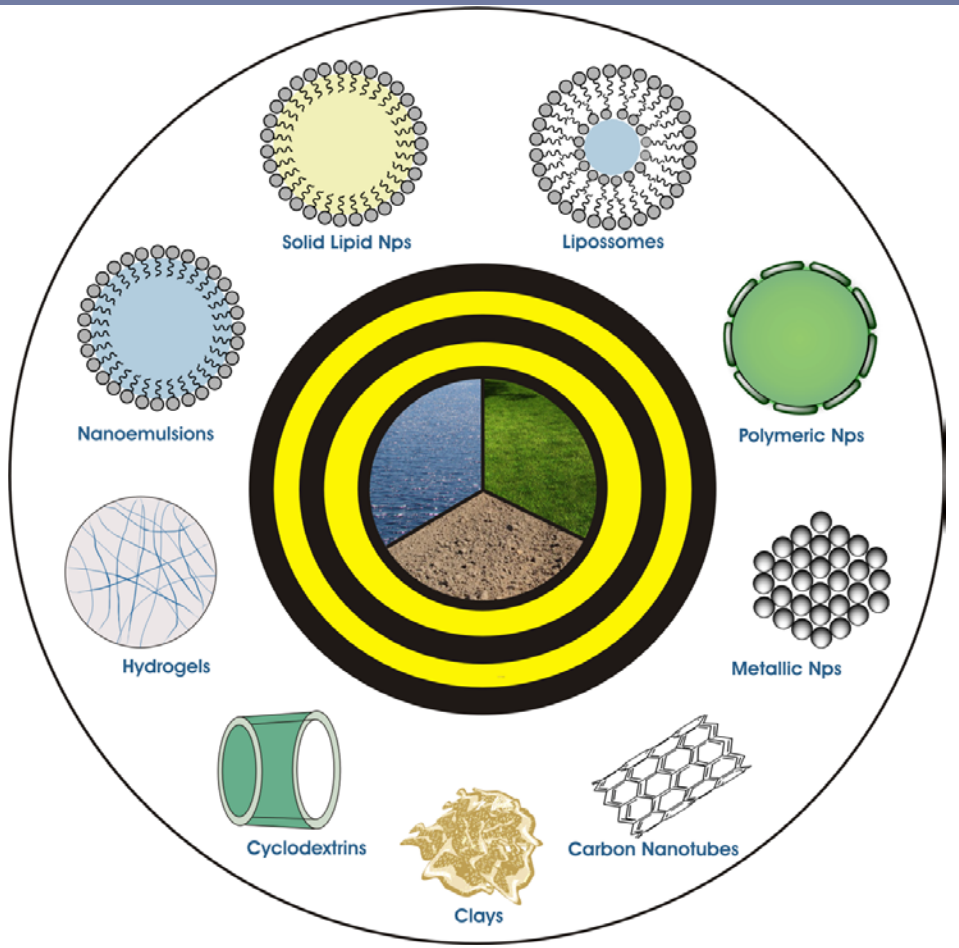
FRACETO, LEONARDO F; GRILLO, Renato ; MEDEIROS, G. A. ; SCOGNAMIGLIO, V. ; REA, G. ; BARTOLUCCI, C. . Nanotechnology in Agriculture: Which Innovation Potential Does It Have?. Frontiers in Environmental Science, v. 4, p. 1-5, 2016.

Our research group

ENVIRONMENTAL NANOTECHNOLOGY LAB

BENEFITS

- ✓ **Increase stability and solubility;**
- ✓ **Modified/targeted release;**
- ✓ **Increase uptake/translocation;**
- ✓ **Reduce the amount of pesticide.**



Schematic representation of several nanocarriers

GRILLO, Renato ; ABHILASH, P. C. ; FRACETO, LEONARDO F . Nanotechnology Applied to Bio-Encapsulation of Pesticides. Journal of Nanoscience and Nanotechnology, v. 16, p. 1231-1234, 2016.

Controlled release systems

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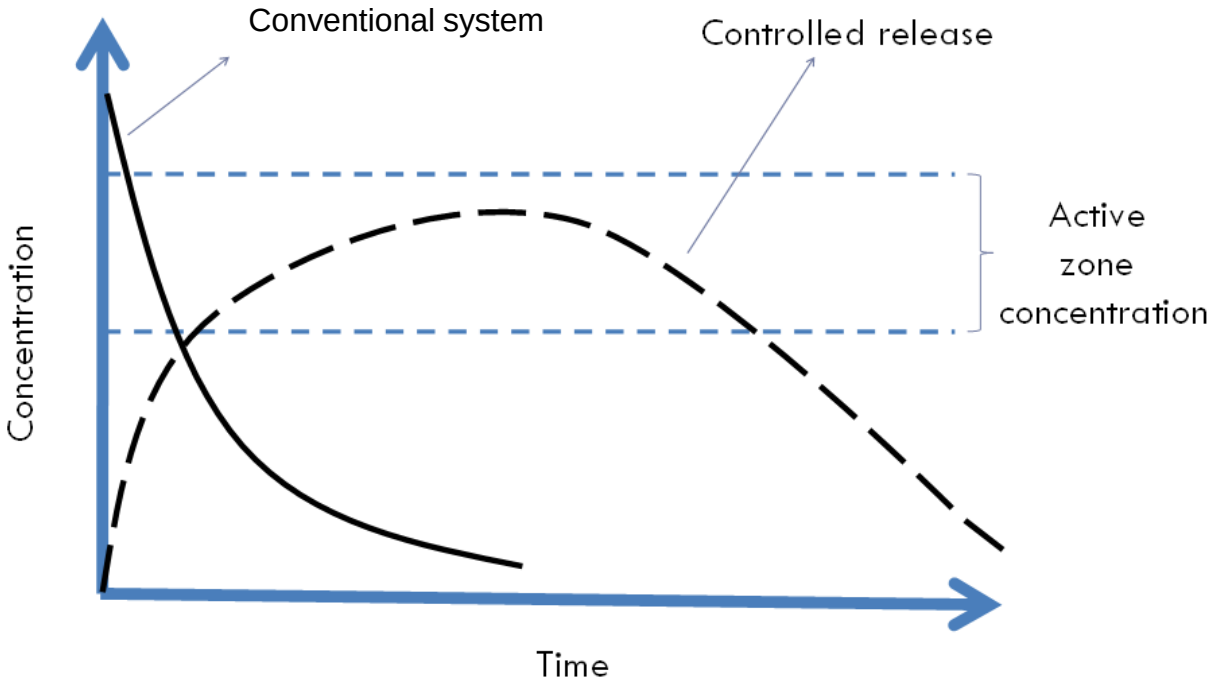
- Modified release systems can:
  - change some bio/availability properties of pesticides
  - modify the pesticides release profile and consequently agricultural management practices
  - decrease the pesticides toxicity and in this way decrease their environmental impacts



Controlled release systems

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- These systems may offer the following advantages for pesticides too:
  - reduction of the amount of chemical substance required for pest control
  - diminished risk of environmental contamination
  - reduction of energy consumption, since fewer applications are needed when compared to conventional formulations
  - increased safety of the people applying the product in the field.

Types of nanocarriers

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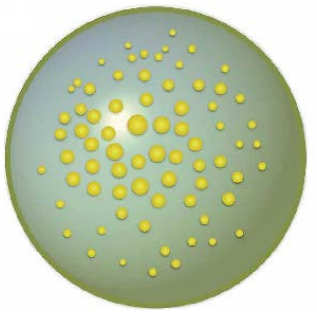
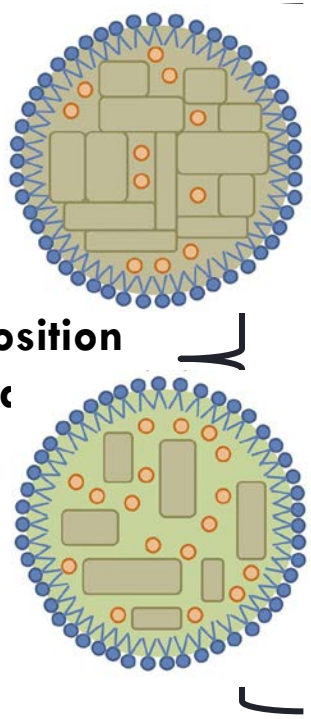
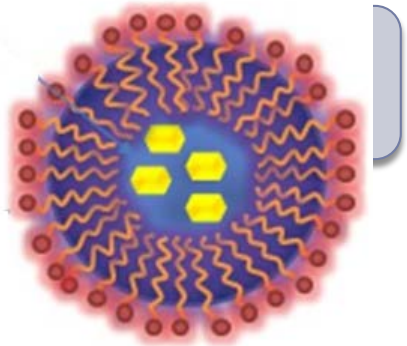


Polymeric micro/nanoparicles

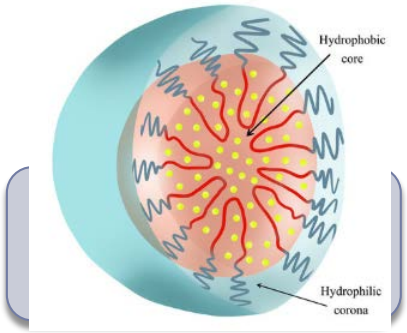


Composition of Mc

Lipidic nanoparticles

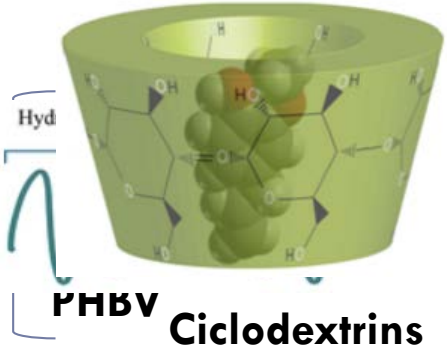


Emulsions



Polymeric micelles

Hidrogels



PHBV Ciclodextrins

Our research group

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- Compounds
  - Herbicides
  - Insecticides
  - Botanicals (insecticides and repellents)
- Plant grown regulator factors

- Nanoparticles
  - Polymeric – PCL, Alginate, Chitosan, zein
  - Lipid

Our strategy

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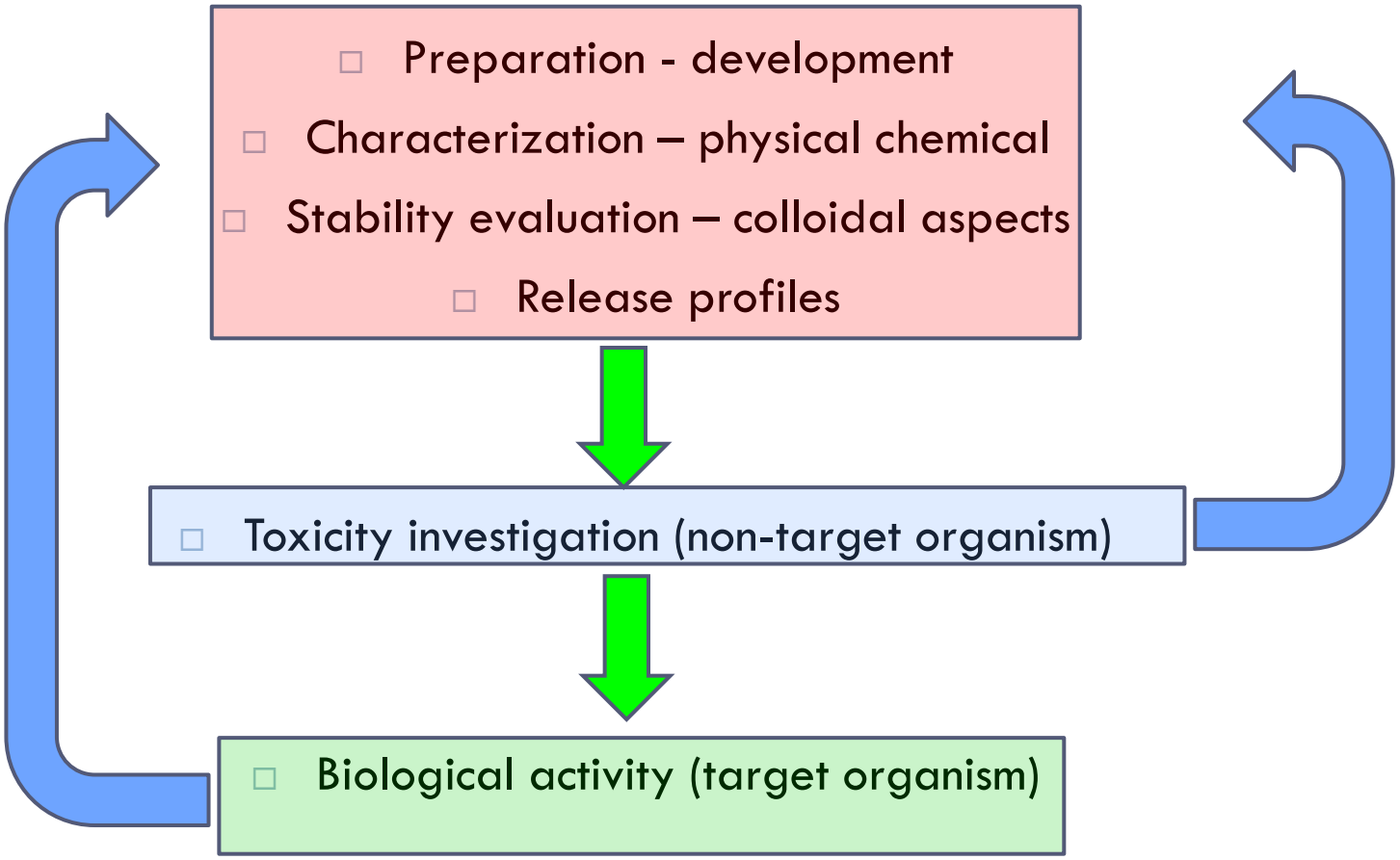


(Motivation)
Example - herbicide

Triazinic herbicide case (2007 - ...)

Journal of Hazardous Materials 231–232 (2012) 1–9

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Poly(ε-caprolactone)nanocapsules as carrier systems for herbicides: Physico-chemical characterization and genotoxicity evaluation

Renato Grillo[a,b], Nathália Zocal Pereira dos Santos[c,d], Cíntia Rodrigues Maryuama[c], André Henrique Rosa[a], Renata de Lima[c], Leonardo Fernandes Fraceto[a,b,*]

Environ Sci Pollut Res (2014) 21:11699–11707
DOI 10.1007/s11356-014-2523-6

14TH EUCHEMS INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT (ICCE 2013, BARCELONA, JUNE 25 - 28, 2013)

Analysing the fate of nanopesticides in soil and the applicability of regulatory protocols using a polymer-based nanoformulation of atrazine

Melanie Kah · Patrick Machinski · Petra Koerner · Karen Tiede · Renato Grillo · Leonardo Fernandes Fraceto · Thilo Hofmann

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Solid Lipid Nanoparticles Co-loaded with Simazine and Atrazine: Preparation, Characterization, and Evaluation of Herbicidal Activity

Jhones Luiz de Oliveira,[†] Estefânia Vangelie Ramos Campos,[†,‡] Camila Morais Gonçalves da Silva,[‡] Tatiane Pasquoto,[§] Renata Lima,[§] and Leonardo Fernandes Fraceto*[,†,‡]

PLOS ONE

RESEARCH ARTICLE

Nanoencapsulation Enhances the Post-Emergence Herbicidal Activity of Atrazine against Mustard Plants

Halley Caixeta Oliveira[1]*, Renata Stolf-Moreira[1], Cláudia Bueno Reis Martinez[2], Renato Grillo[3,4], Marcelo Bispo de Jesus[5], Leonardo Fernandes Fraceto[3,4]*

Journal of Nanoscience and Nanotechnology
Vol. 13, 1–7, 2013

Ecotoxicological Evaluation of Poly(Epsilon-Caprolactone) Nanocapsules Containing Triazine Herbicides

Z. Clemente[1,2,†], R. Grillo[2,3,†], M. Jonsson[1], N. Z. P. Santos[4], L. O. Feitosa[4], R. Lima[4], and L. F. Fraceto[2,3,*]

frontiers in Chemistry

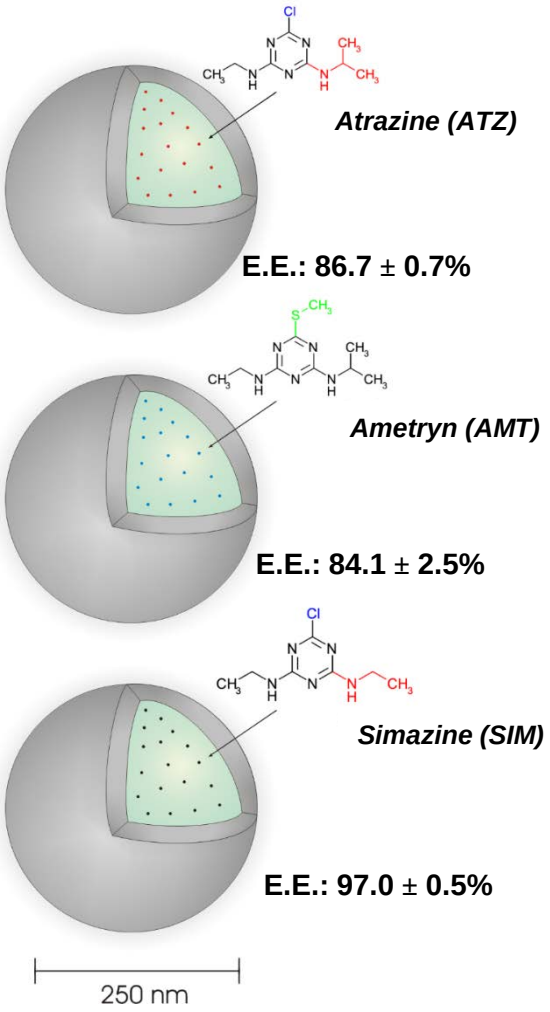
ORIGINAL RESEARCH

Evaluation of the side effects of poly(epsilon-caprolactone) nanocapsules containing atrazine toward maize plants

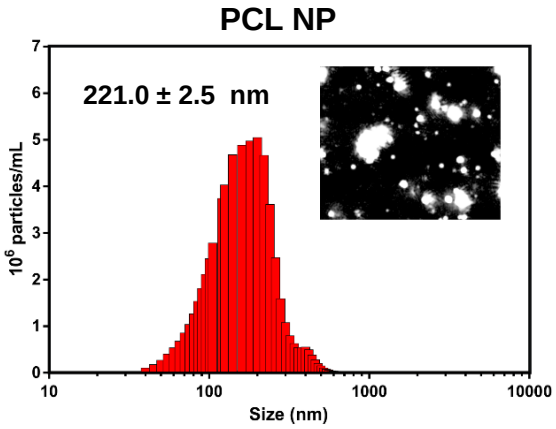
Halley C. Oliveira[1]*, Renata Stolf-Moreira[1], Cláudia B. R. Martinez[2], Gustavo F. M. Sousa[1], Renato Grillo[3,4], Marcelo B. de Jesus[5] and Leonardo F. Fraceto[4,3]*

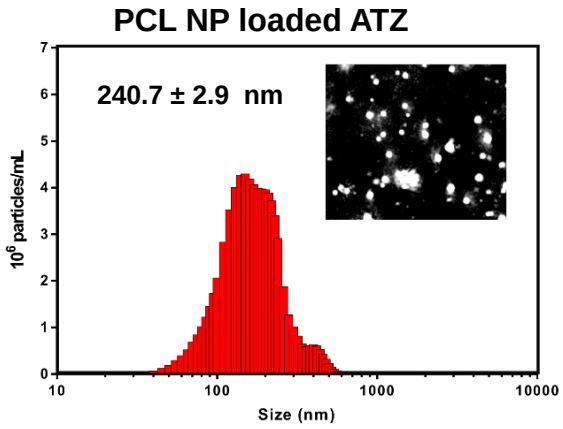
Nanoparticles with triazinic herbicides

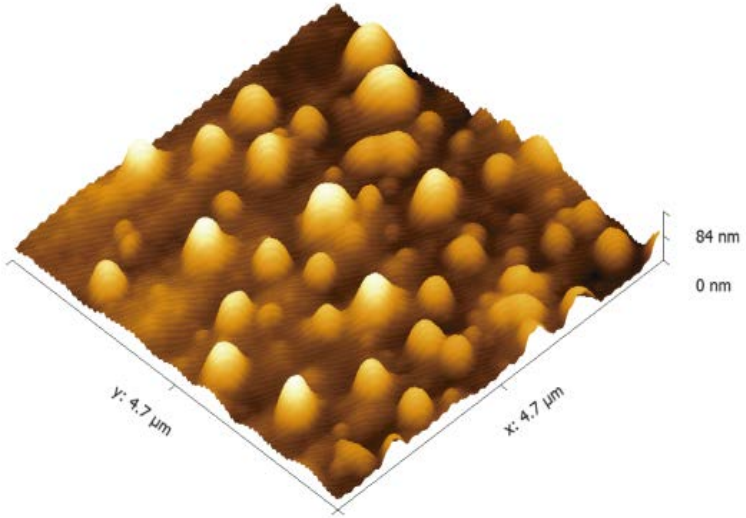
ENVIRONMENTAL NANOTECHNOLOGY LAB



Nanopreciptation Method

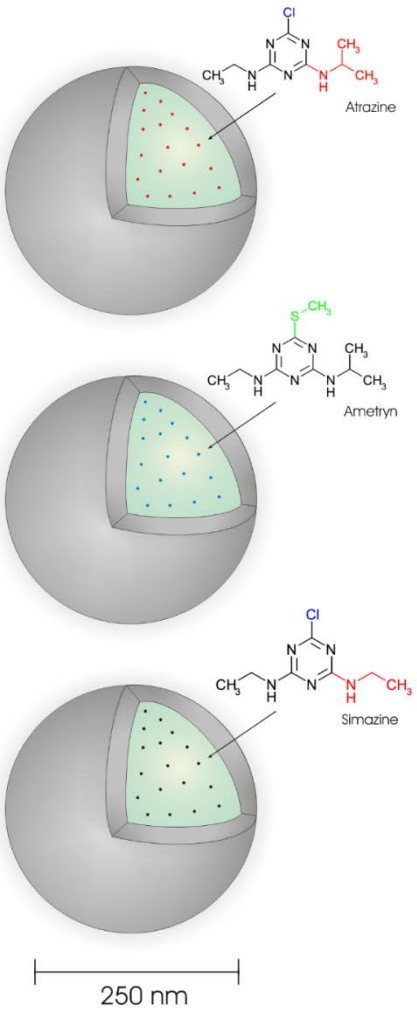


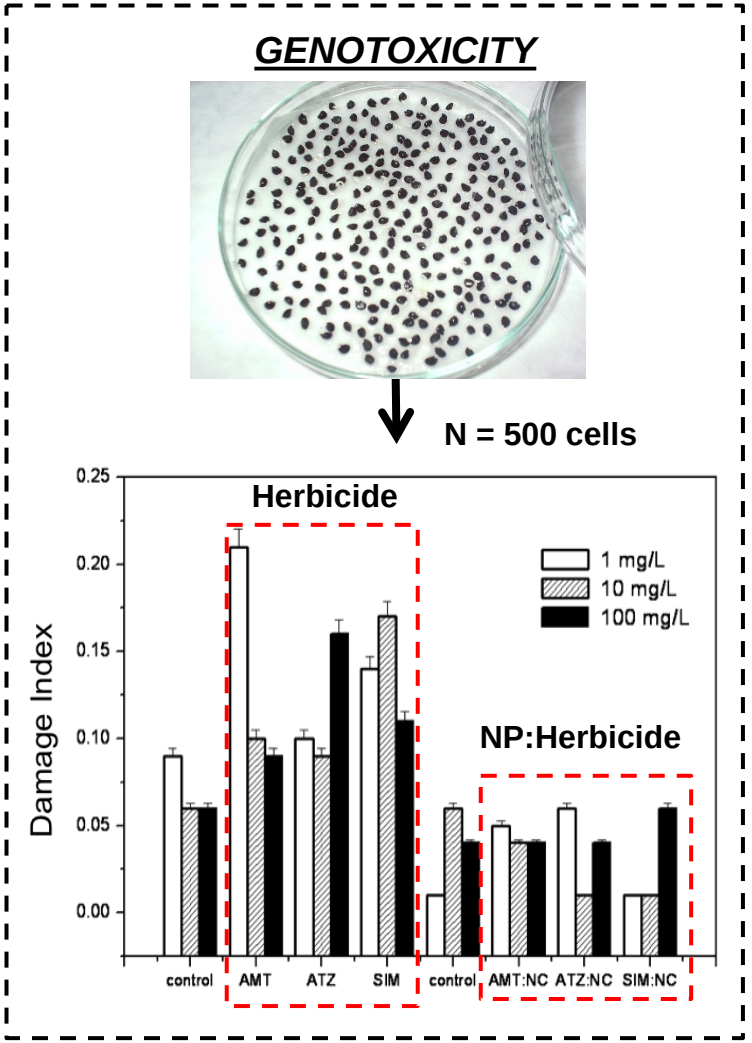




Grillo et al. J. Haz. Mat. 231-232 (2012) 1-9; Oliveira et al. PLoS ONE 10(7): e0132971

Genotoxicity





Target organism

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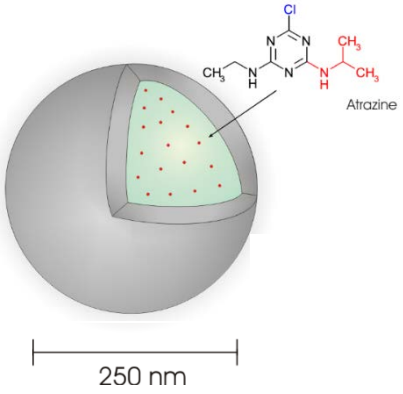
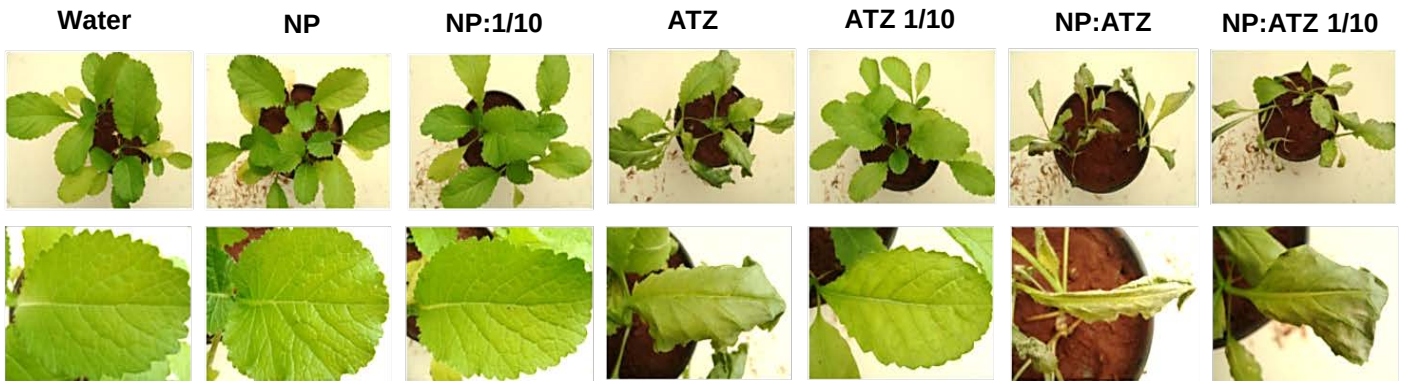
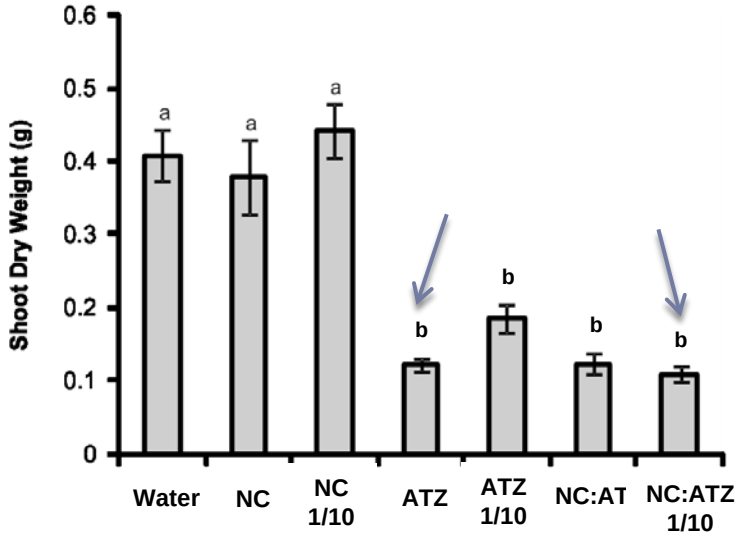
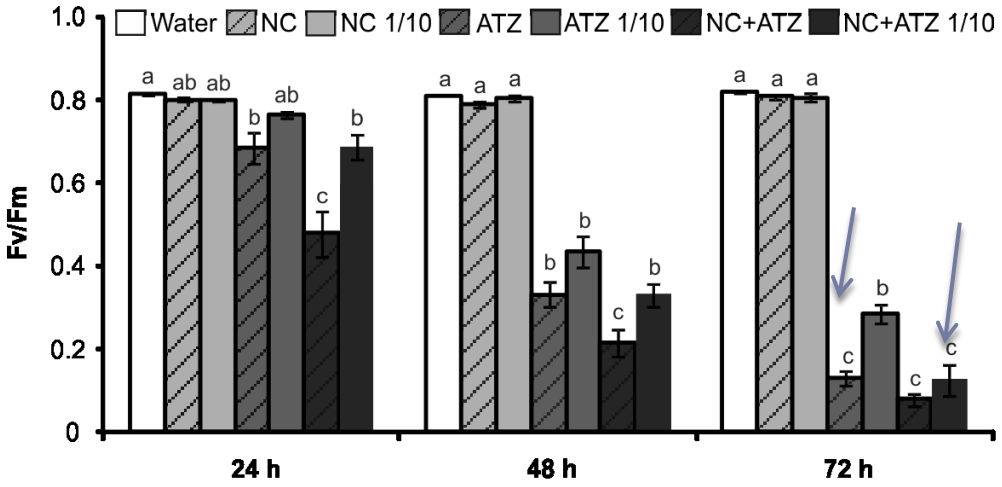






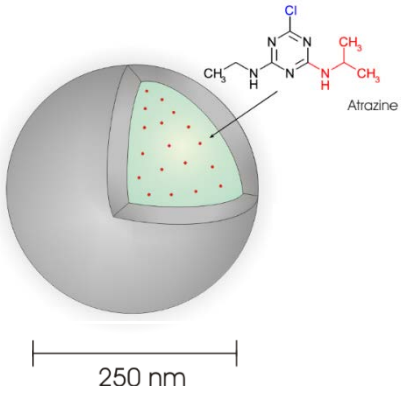
Shoot dry weights of *B. juncea* plants, n=16.

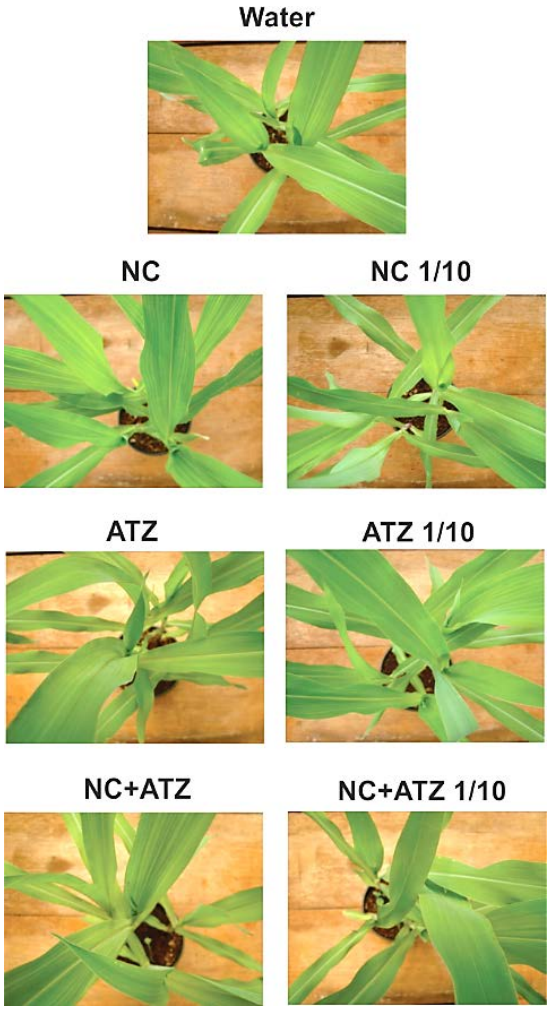


Maximum photosystem II quantum yields of *B. juncea* plants, n = 5.

Non-target organism

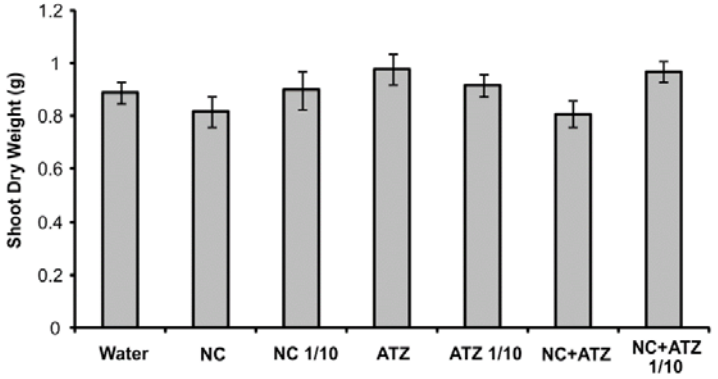
ENVIRONMENTAL NANOTECHNOLOGY LAB



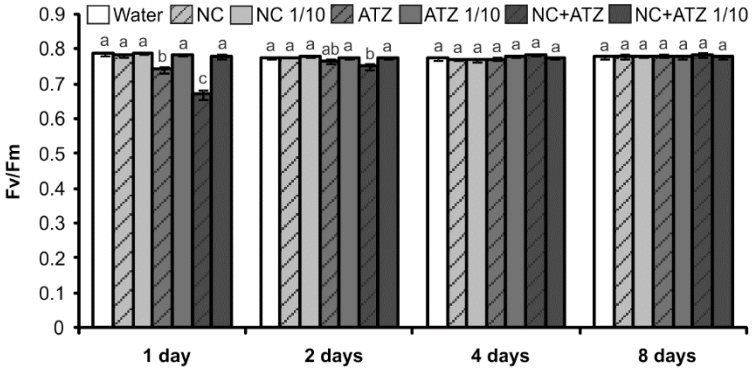


Symptom evolution in *Zea mays* L leaves.

NO EFFECT



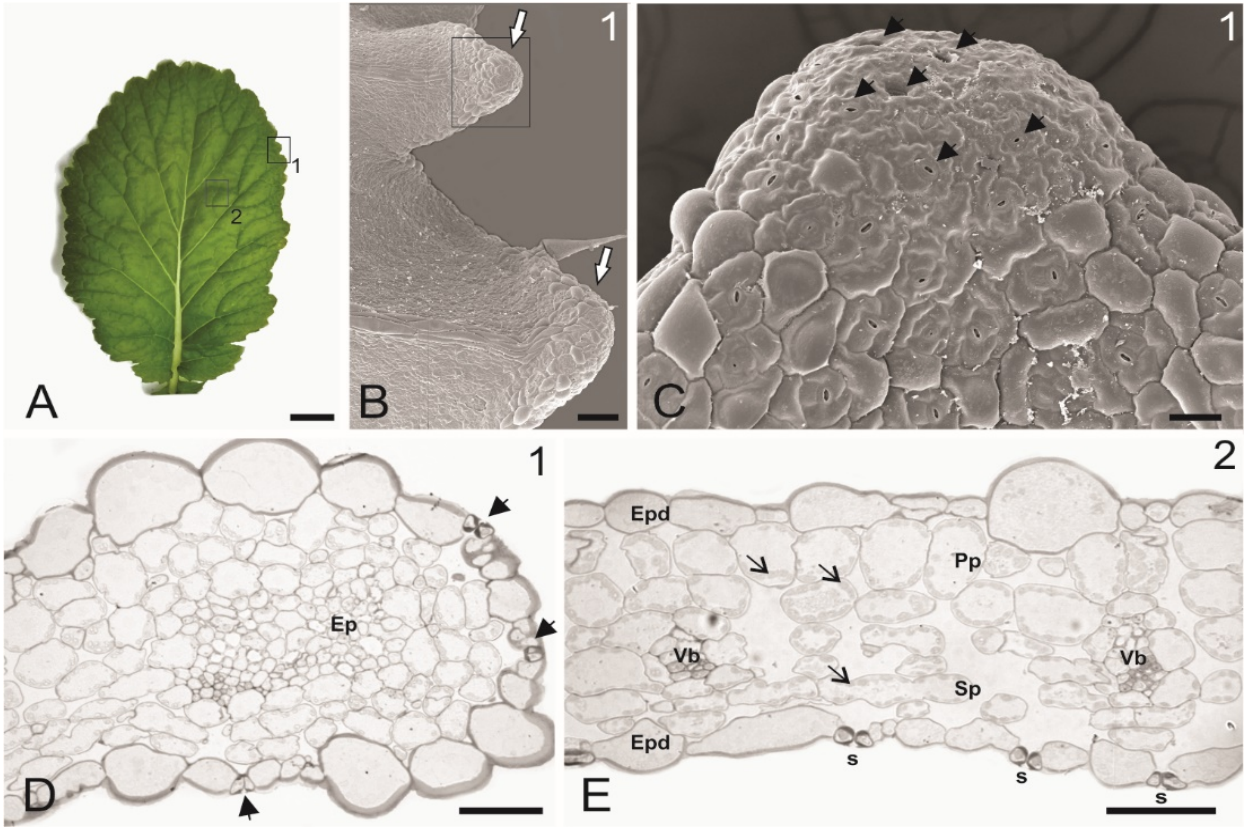
Shoot dry weights of *Zea mays* L. plants.



Maximum photosystem II quantum yields of *Zea mays* L.

Mechanism of action – labelled particles

ENVIRONMENTAL NANOTECHNOLOGY LAB



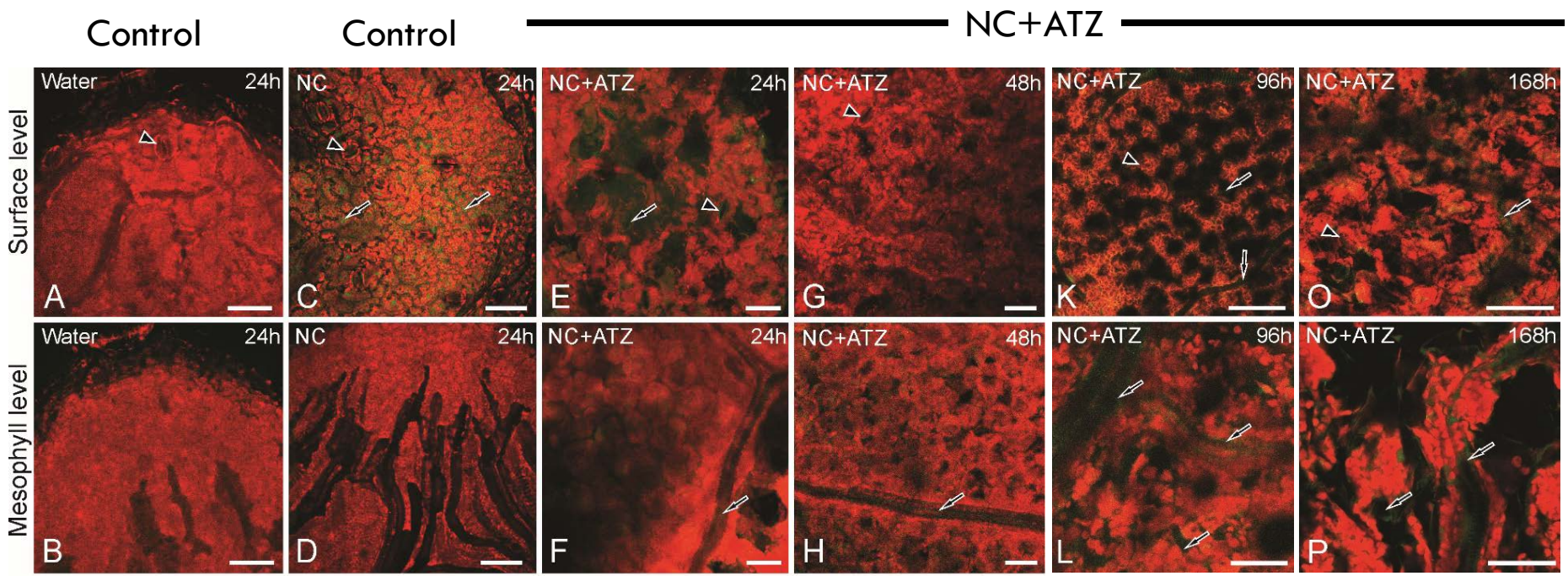
hydathode

mesophyll

Microscopic characterization of a healthy *Brassica juncea* leaf, showing the hydathode (1) and mesophyll (2) regions. A–D. Hydathodes on the leaf edge. Arrows in B indicate hydathodes. C. Detail of the B inset, arrows indicate water pores. D. Longitudinal section of a hydathode on the leaf edge, showing its anatomical structure. E. Transverse section of the middle region of the leaf blade (2), arrows indicate chloroplasts in the chlorophyll parenchyma. Ep = epithem, Epd = epidermis, Pp = palisade parenchyma, s = stomata, Sp = spongy parenchyma, Vb = vascular bundle.

Mechanism of action

ENVIRONMENTAL NANOTECHNOLOGY LAB



Confocal micrographs of hydathode regions on a *Brassica juncea* leaf, showing nanoparticle penetration after incubation with water, nanocapsules (NC), or nanocapsules containing atrazine at 0.1 mg mL^{-1} (NC + ATZ).

Arrowheads indicate stomata on the leaf surface and arrows indicate the green fluorescent signal of the dye.

Reality? Long way....

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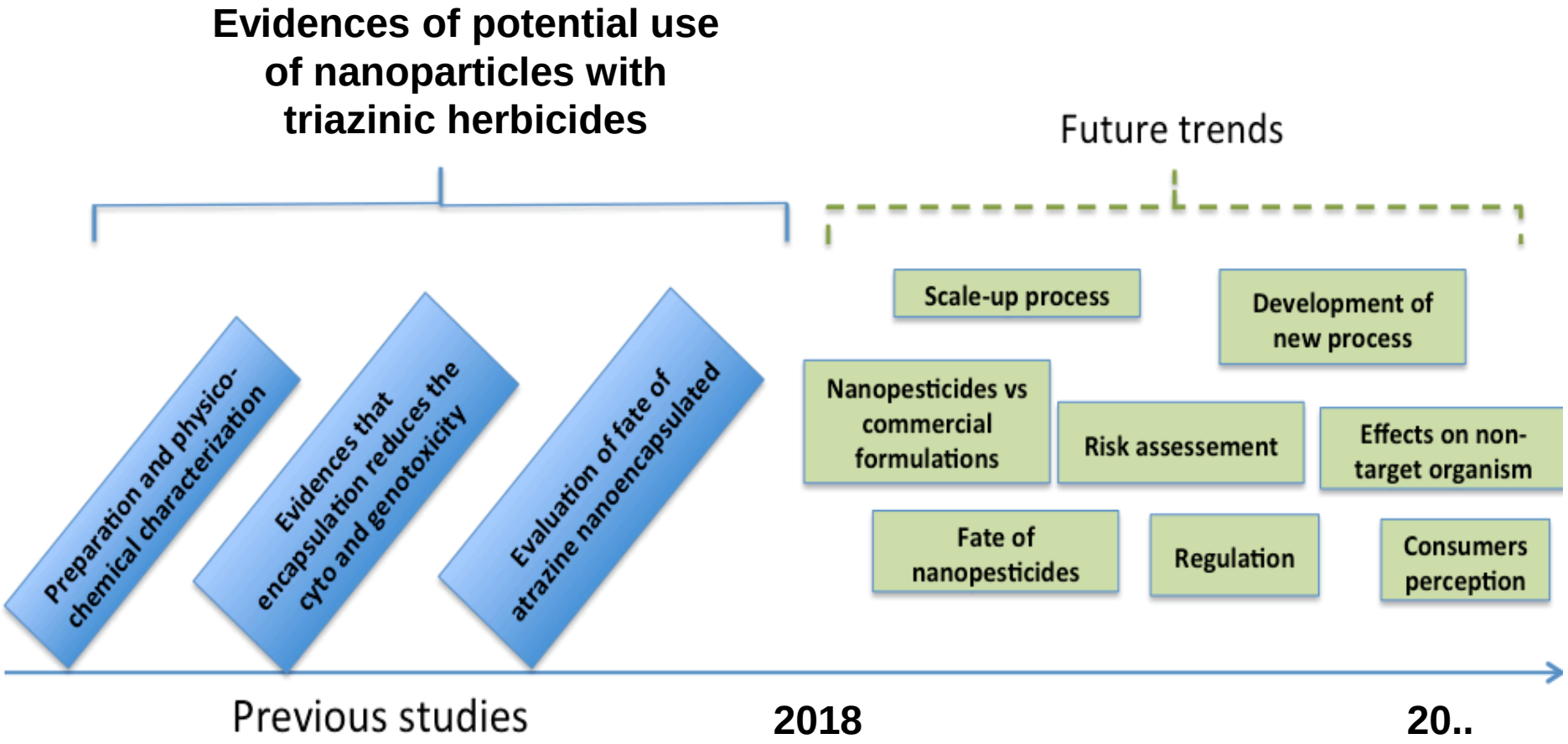

In progress...

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Mechanism of action in plants

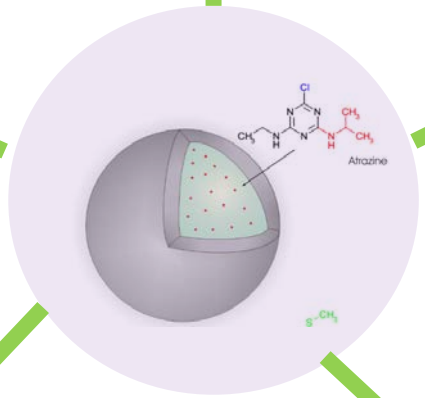
Dra. Juliana Mayer

UNICAMP

Biosensor for nanoatrazine

Dr. Viviana Scognamiglio

National Research Council of Italy



Deep characterization of the nanoparticles/flow chemistry synthesis

Dr. Valeria Arrighi
Dr. Filipe Vilela

HERIOT WATT UNIVERSITY

Exposure (lung)

Dr. Terry Tetley

Imperial College London

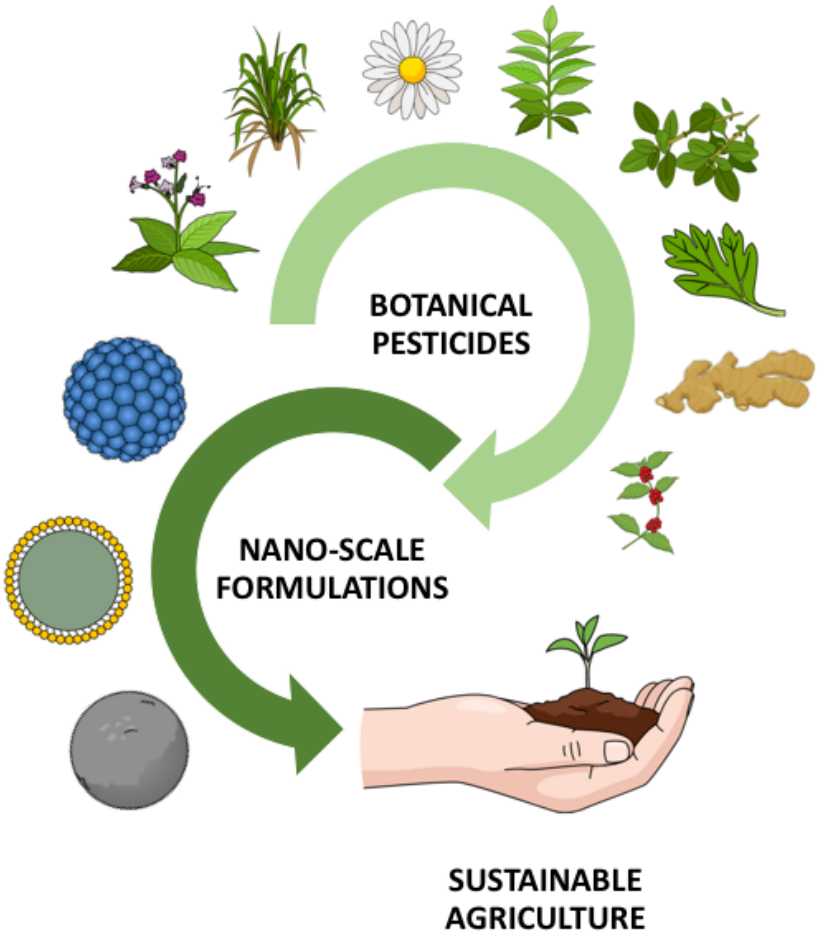
Ecotoxicity

Dr. Monica Amorim

universidade de aveiro

Sustainable Agriculture

ENVIRONMENTAL NANOTECHNOLOGY LAB



OLIVEIRA, J.L.; CAMPOS, E. V. ; FRACETO, L F . Recent developments and challenges for nano-scale formulation of botanical pesticides for use in sustainable agriculture. JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY , v. 66, p. 8898-8913, 2018.

Sustainable Agriculture

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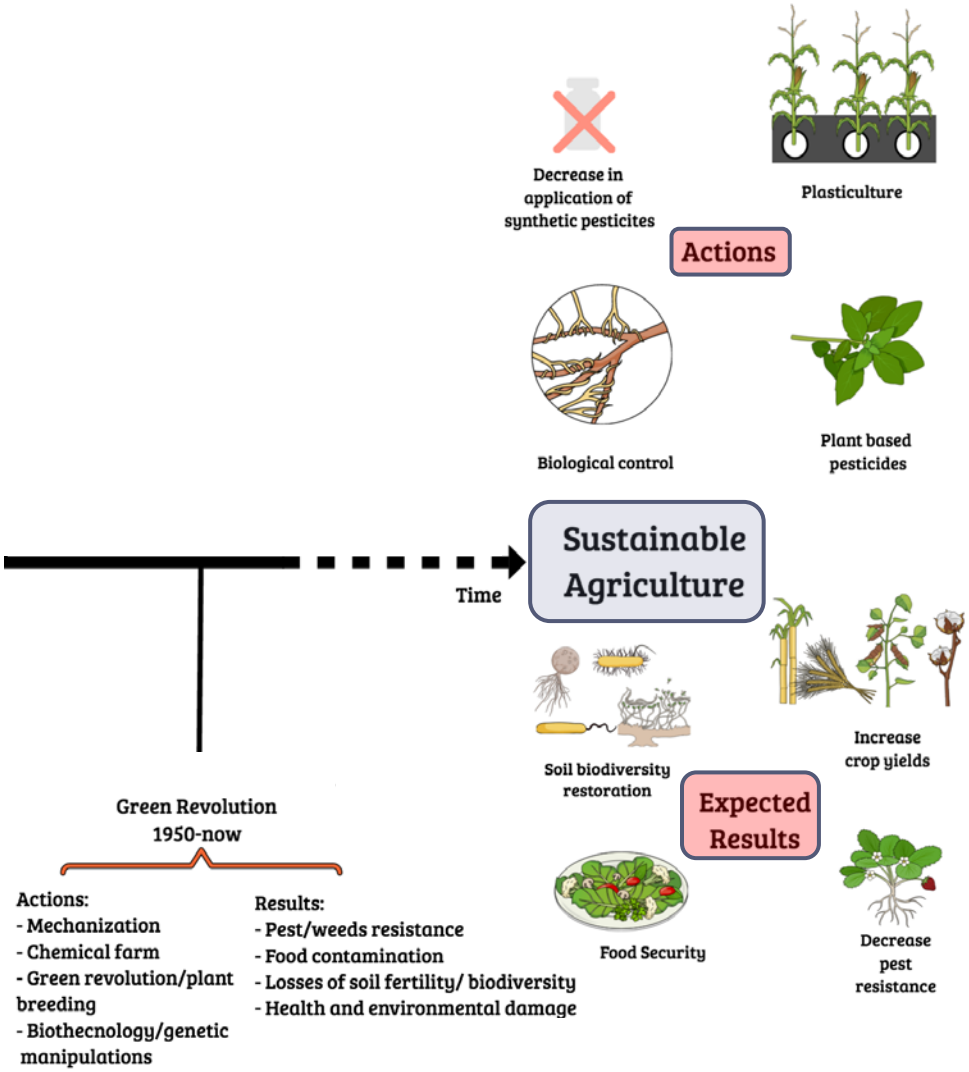
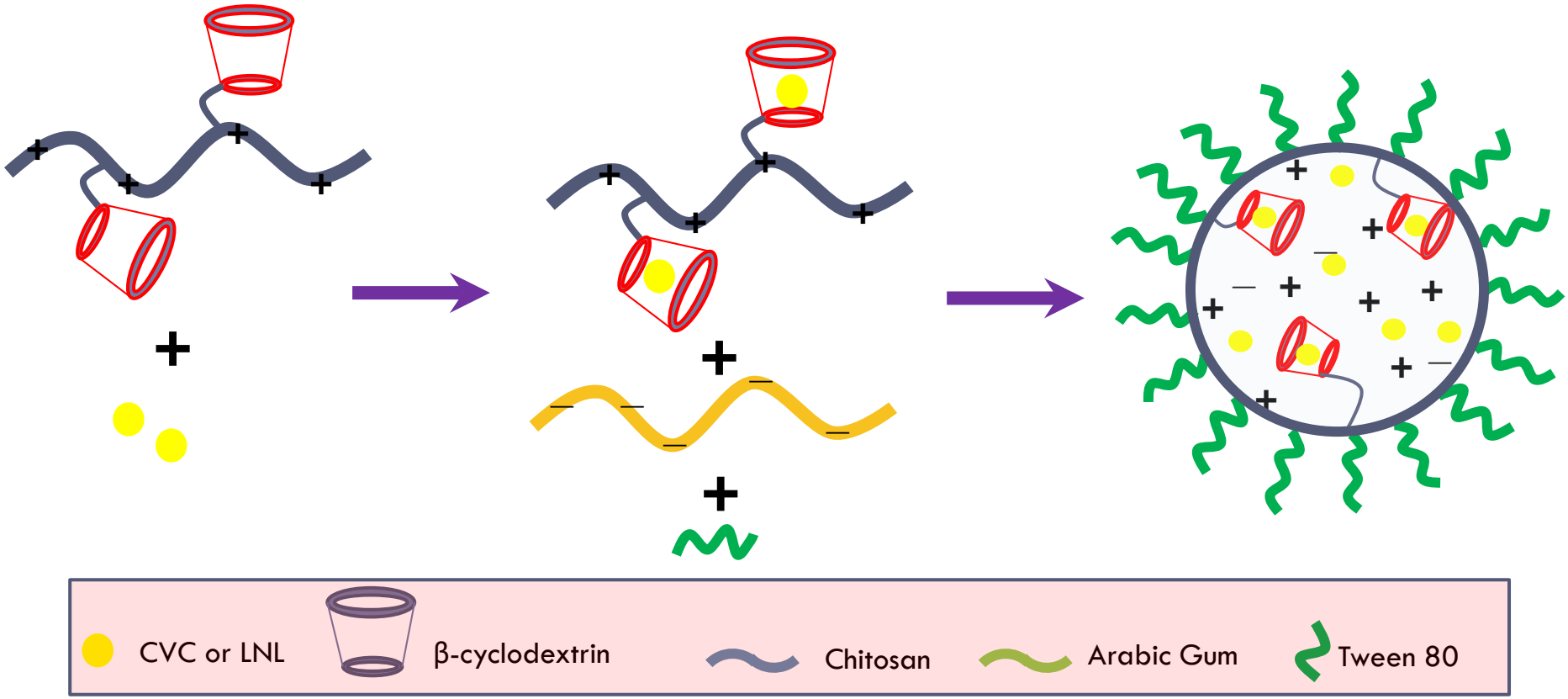


Botanicals insecticides

ENVIRONMENTAL NANOTECHNOLOGY LAB

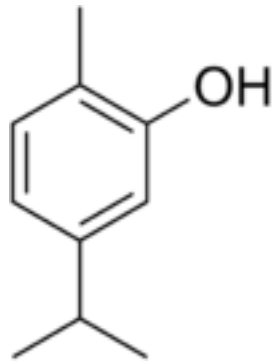
Chitosan-β-cyclodextrin nanoparticles for sustained release of carvacrol and linalool for applications in agriculture



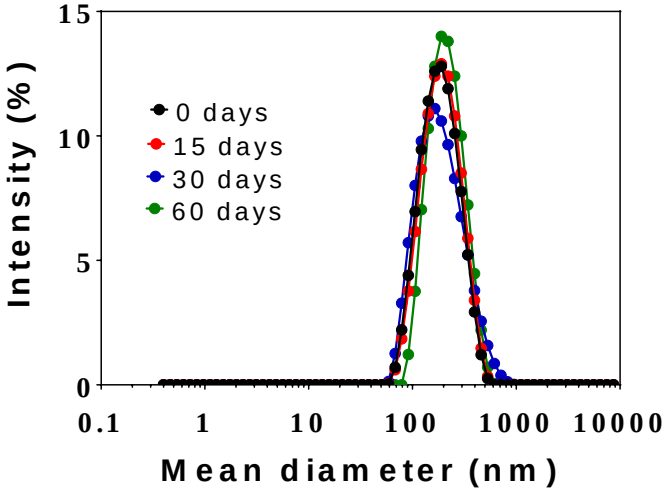
Avadi et al., Nanomedicine: nanotechnology, biology and medicine, 6, 58 (2010); Tan et al., Anal. Methods 4, 2784 (2012)

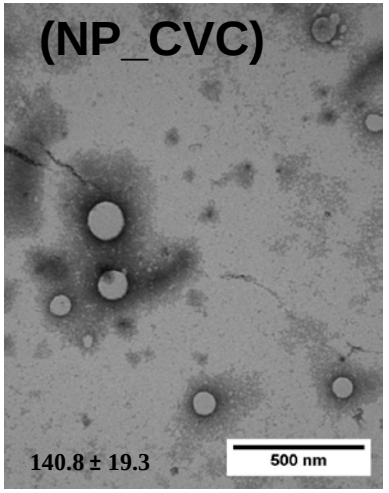
Chitosan nanoparticles

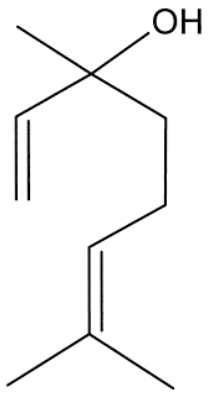
ENVIRONMENTAL NANOTECHNOLOGY LAB



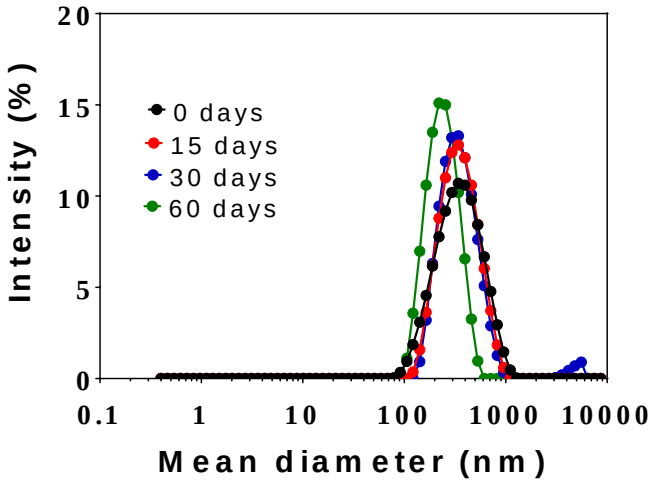
Carvacrol

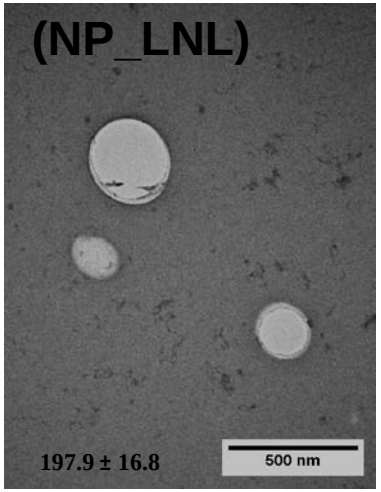






Linalool





CAMPOS, et al. Scientific Reports, v. 8, p. 2067, 2018.

Toxicity (cyto and phyto)

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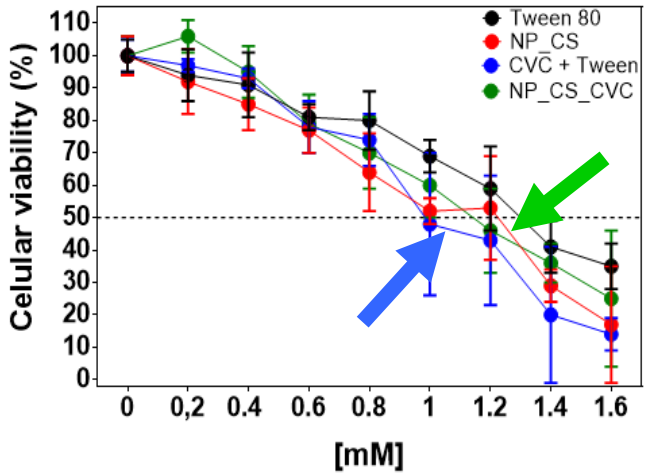
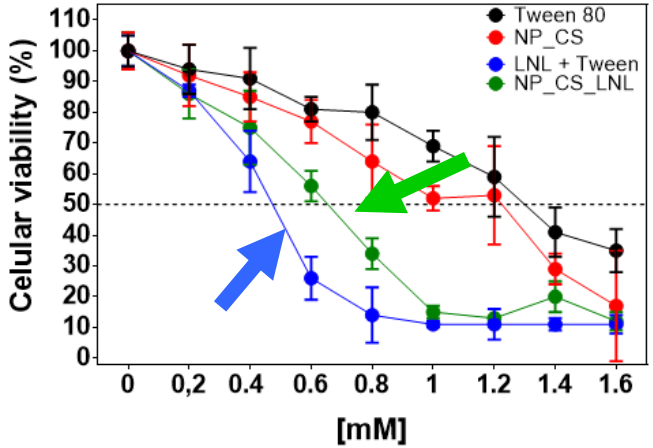
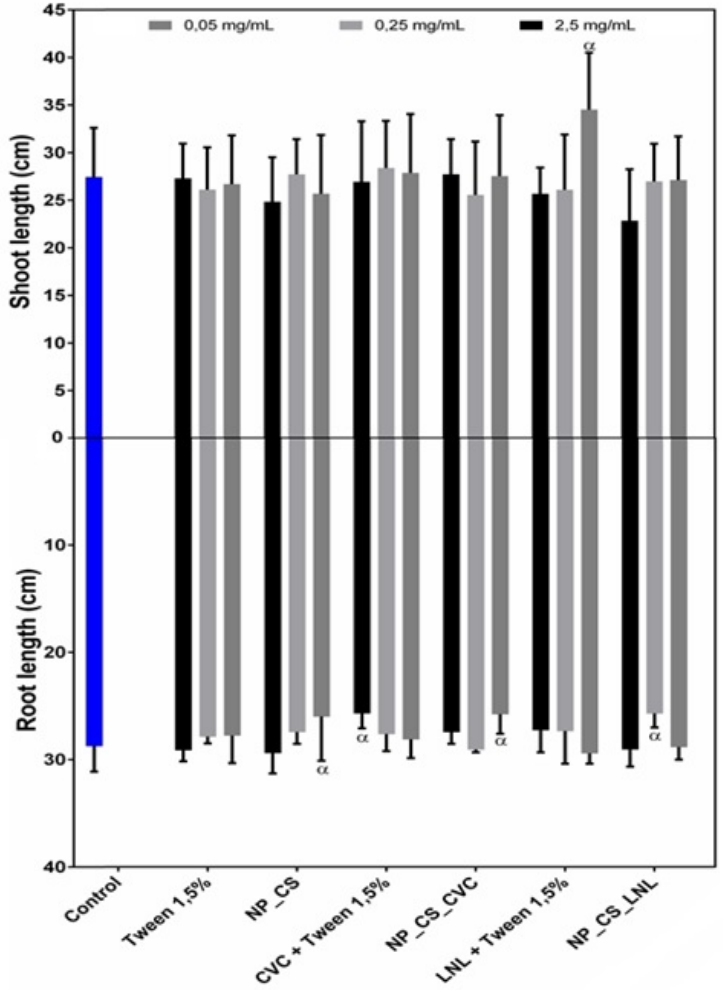
3T3 cells







Encapsulation increased insecticide IC_{50}

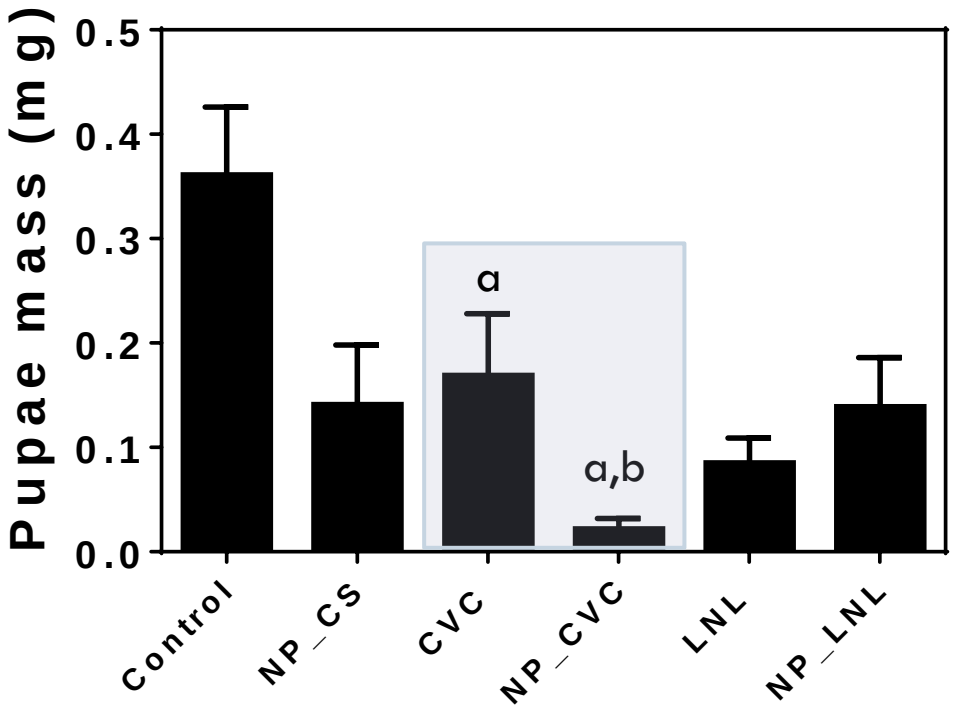
No phytotoxicity in beans

CAMPOS, et al. Scientific Reports, v. 8, p. 2067, 2018.

Insecticide activity

ENVIRONMENTAL NANOTECHNOLOGY LAB

Helicoverpa armigera



Agricultural pest of major global importance

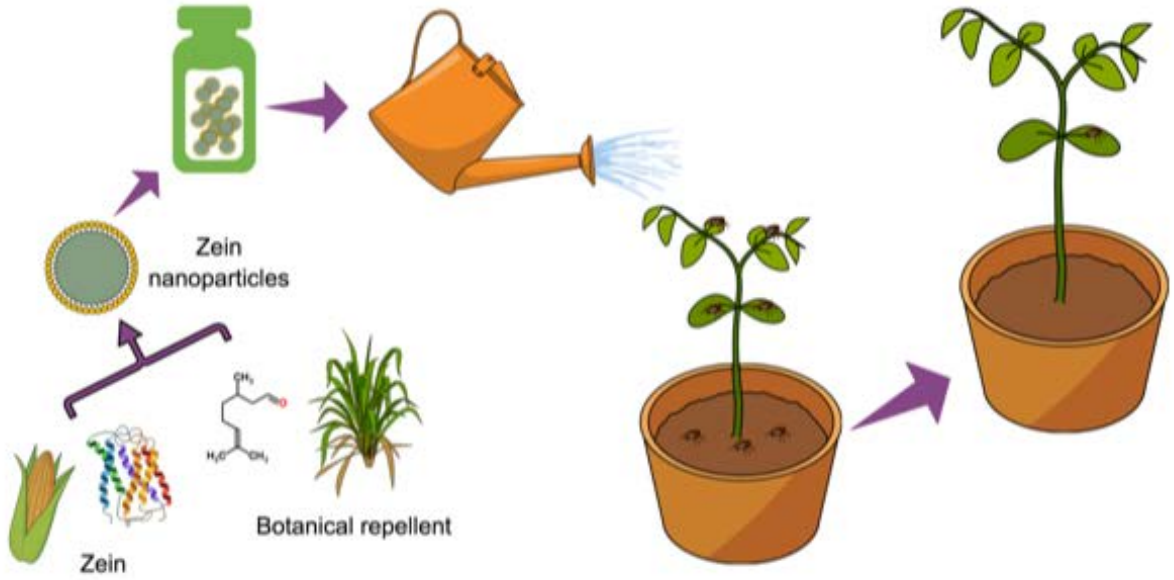
Its occurrence has already been recorded in more than 200 species of host plants, cultivated and wild

Feed on leaves, fruits and pods
Adapting to seasonal climate changes

Botanicals repellents – Case I

ENVIRONMENTAL NANOTECHNOLOGY LAB

Zein nanoparticles as eco-friendly carrier systems for botanical repellents aiming sustainable agriculture



Oliveira et al., Journal Agricultural and Food Chemistry, v.66, 1330-1340, 2018.

Zein nanoparticles

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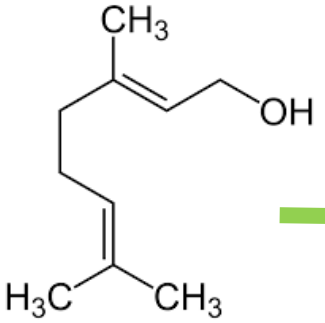
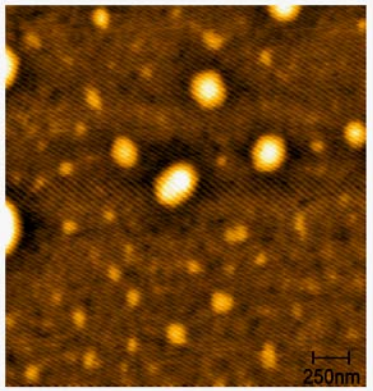
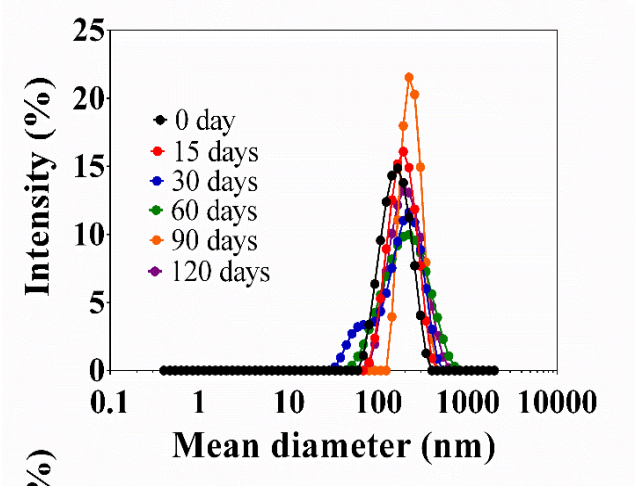
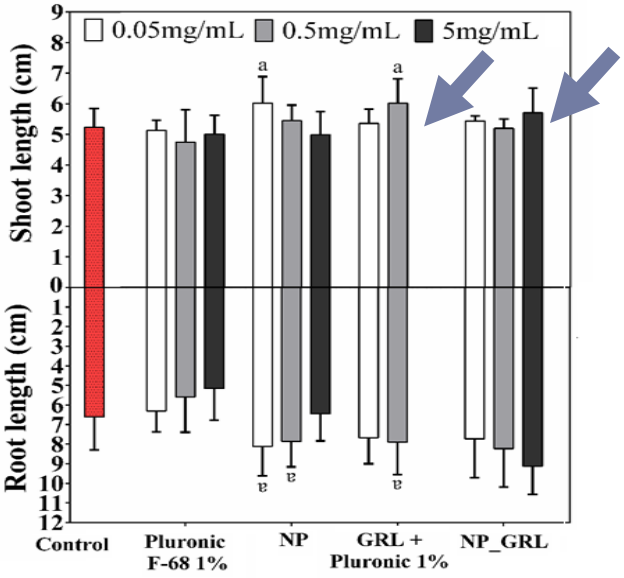
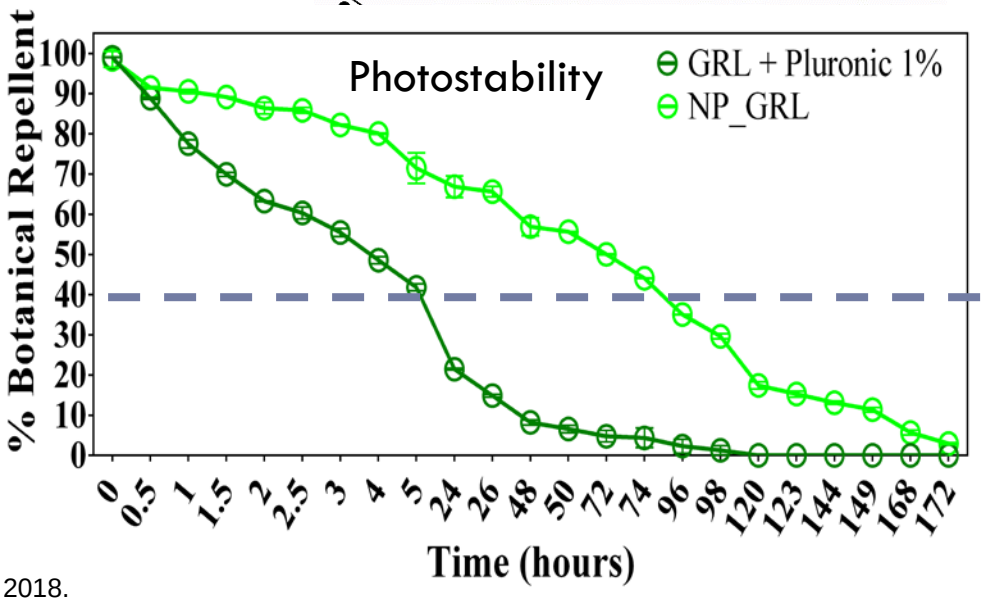


geraniol









Oliveira et al., Journal Agricultural and Food Chemistry, v.66, 1330-1340, 2018.

Biological Activity

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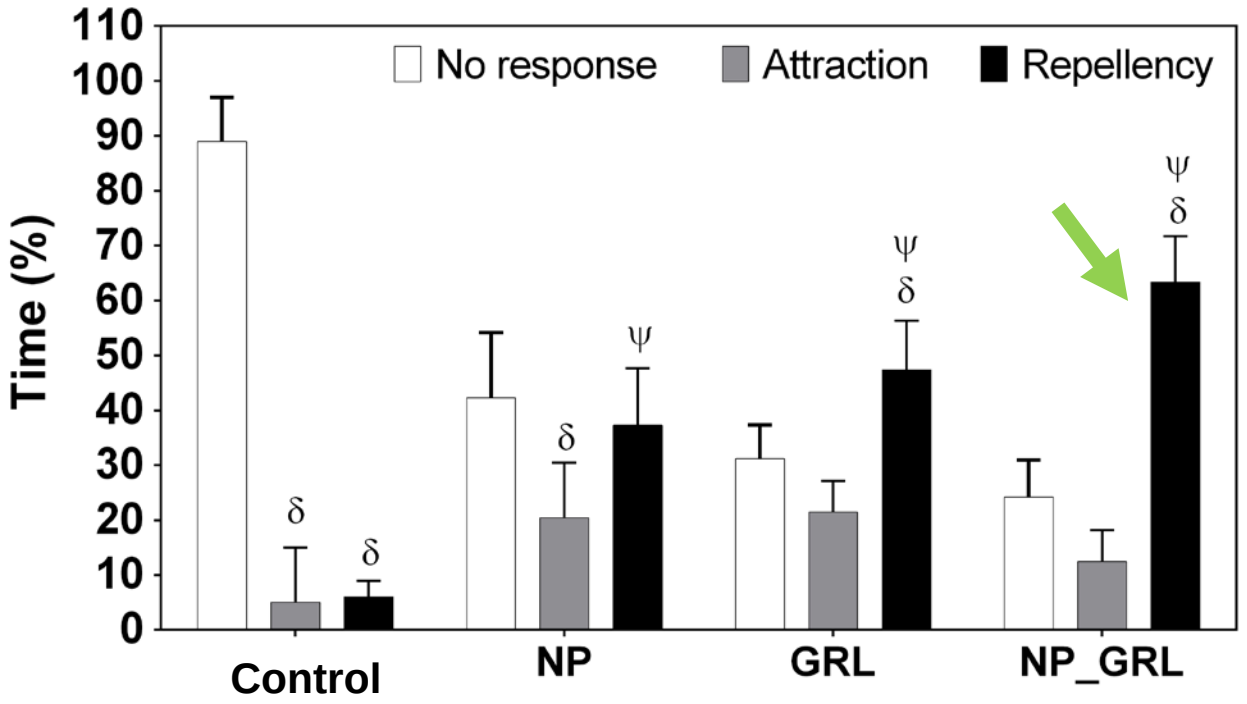
Whitefly (*Bemisia tabaci*)

Large variety of host plants

↓

Feeds on plant sap and introduces viruses

↓



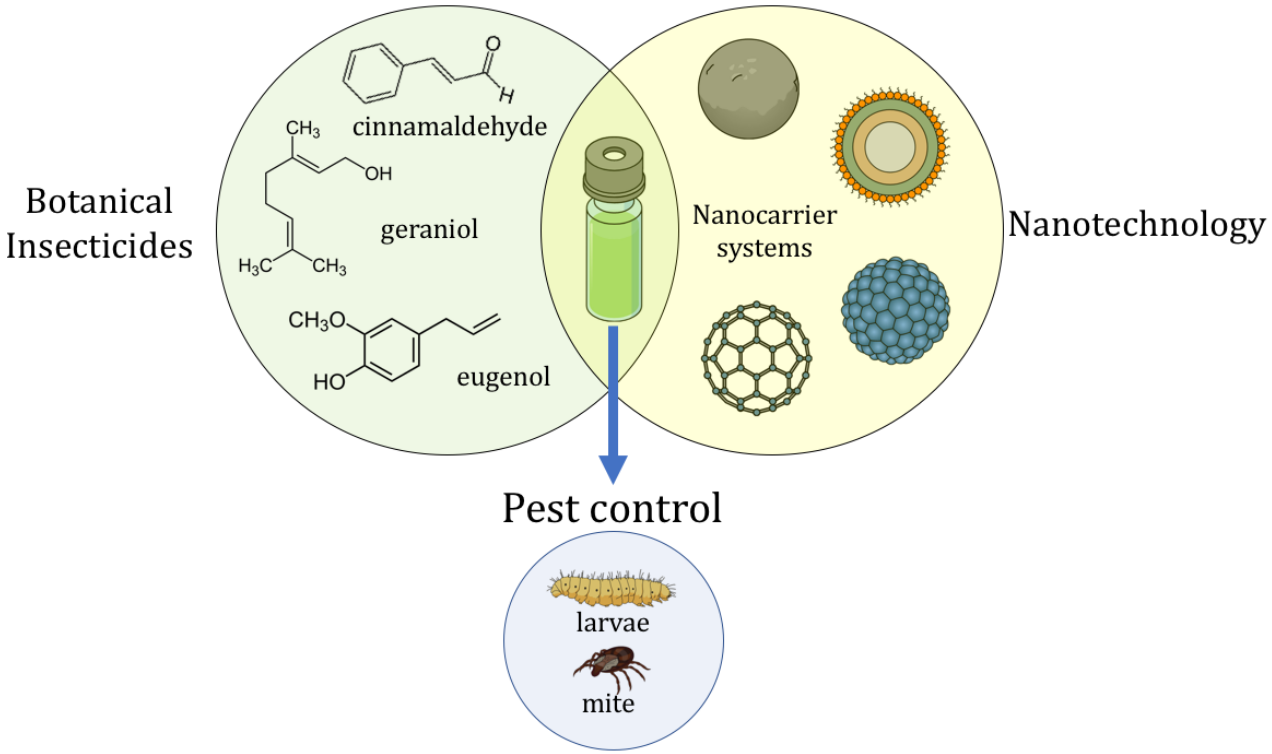
Response of the whitefly (*Bemisia tabaci*) after 4-way olfactometer assay.

Oliveira et al., Journal Agricultural and Food Chemistry, v.66, 1330-1340, 2018.

Botanical Repellents – Case II

ENVIRONMENTAL NANOTECHNOLOGY LAB

Convergence of botanical compounds with nanotechnology for effective pest control systems



Characterization

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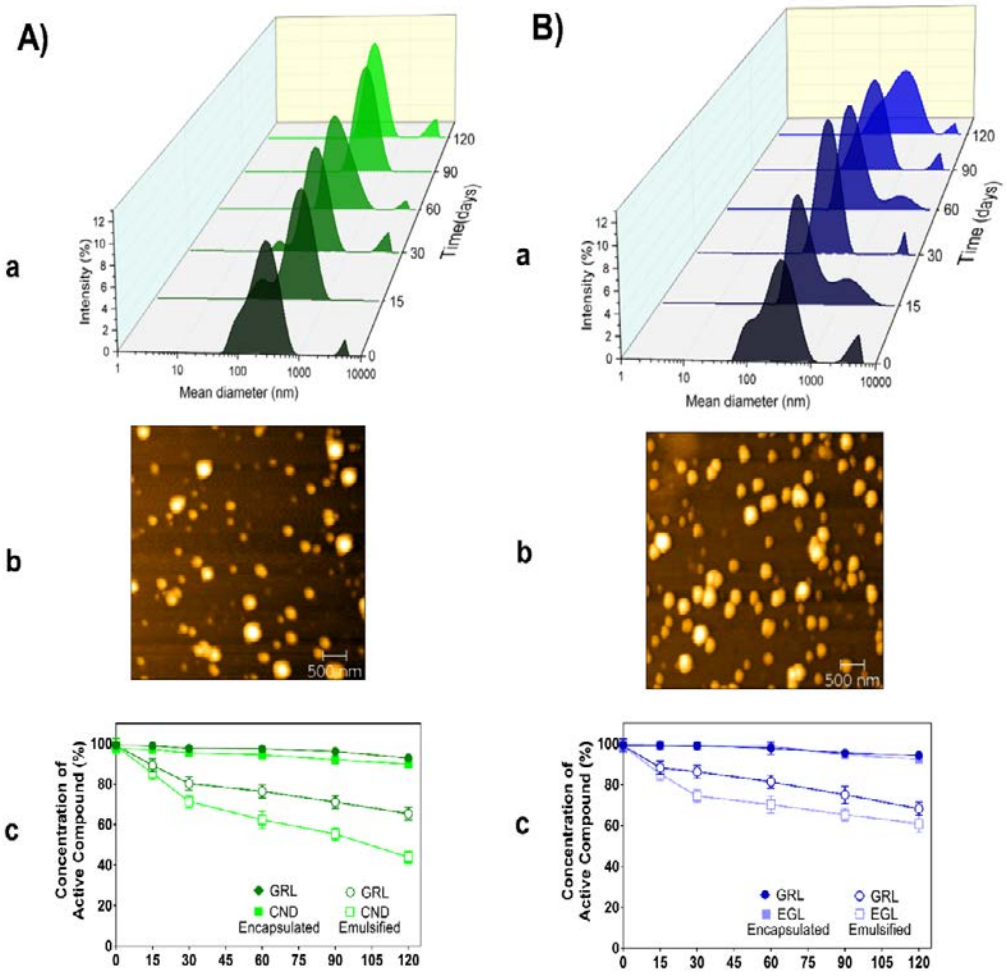

Biological Activity

ENVIRONMENTAL NANOTECHNOLOGY LAB

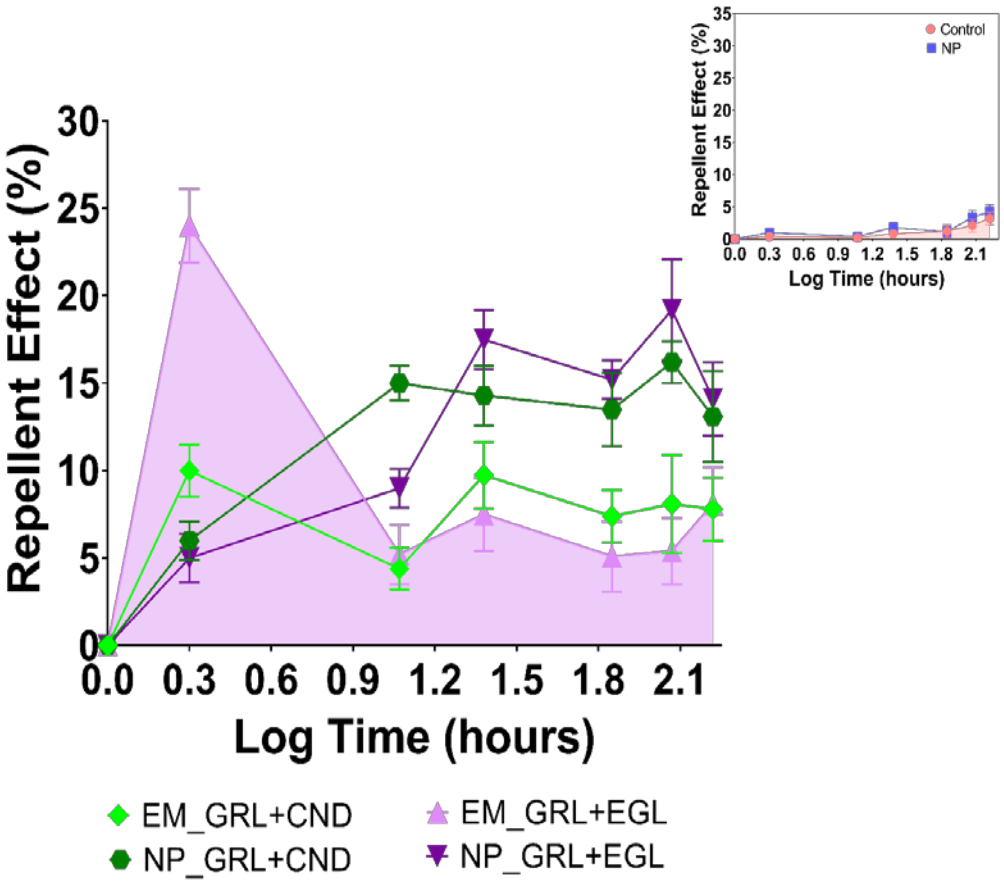

Table 1: Area values on the curve for the repellent activity assays of the formulations containing the mixture of the active compounds, as well as the respective controls.

Formulation	Area under the curve (repellency x time)
Control	1.7 ± 0.3
NP	2.8 ± 0.4
EM_GRL+EGL	19.9 ± 1.4 [a]
NP_GRL+EGL	24.2 ± 1.1 [a,b]
EM_GRL+CND	16.2 ± 1.1 [a]
NP_GRL+CND	25.5 ± 0.9 [a,c]

Botanicals attractives

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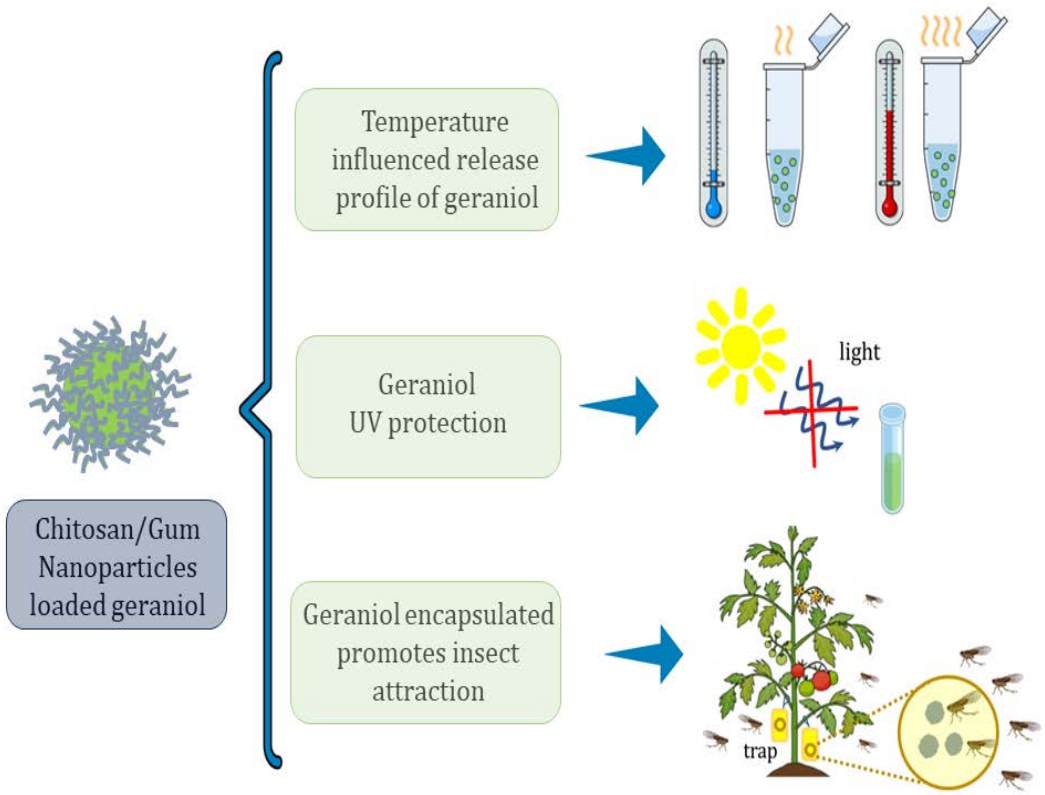
Geraniol encapsulated in chitosan/gum arabic nanoparticles: a promising system for pest management in sustainable agriculture



Oliveira et al., Journal Agricultural and Food Chemistry, v.66, 5325-5334, 2018.

Biological Acitivity

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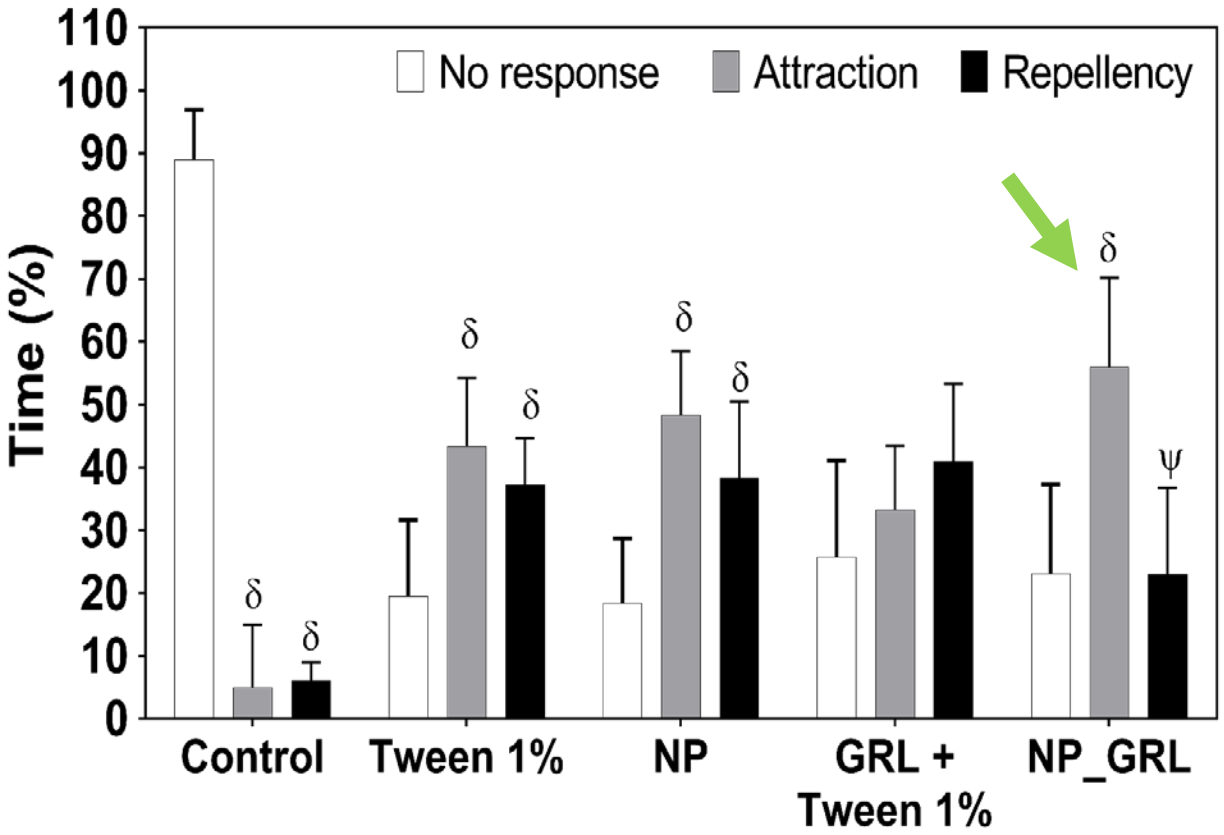

Oliveira et al., Journal Agricultural and Food Chemistry, v.66, 5325-5334, 2018.

Conclusions and perspectives

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- Nanotechnology has potential to be used in agriculture (in special in sustainable) since:
  - Toxicity (cyto and phyto) studies showed that the encapsulation decreased the active ingredient toxicity
  - Botanical insecticides/repellents and nanotechnology showed promising results in target organisms

However.... We need more and more and more regarding to non target organisms toxicity studies, fate of pesticides, mechanism of action, food security etc.

Challenges

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- Production costs
- Scale-up
- Regulatory markers
- Adequate techniques/methodology to evaluate the environmental risks
- Fate of nanomaterials
- Mechanisms of action and toxicity of biopesticides based on nanomaterials

Acknowledgments

ENVIRONMENTAL NANOTECHNOLOGY LAB

People:
Dr. Renata de Lima (University of Sorocaba)
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Dr. Daniel Andrade (Unesp/Jaboticabal)

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Daniele Abrantes (Unesp)

FAPESP

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

CAPES

Profa. Tatiana Volova

СИБИРСКИЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ
SIBERIAN FEDERAL UNIVERSITY

Unesp

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- Academic Programs
- Graduate Studies
- Research
- International students
- Unesp in the community
- Publishing House
- Technology Innovation Agency
- News

Página inicial › Inglês

Home

Unesp offers 20 free international courses in four different areas

Courses are offered in areas where Unesp has a high level of scientific competence: Agriculture, Alternative Energy, Dentistry and Literature & Linguistics.

British professor wants to expand research on brazilian migrants

At Unesp Rio Claro, Cathy McIlwane, of the Queen Mary University of London, is planning a joint research about the impact of the migration in the local families.

Ranking lists Unesp as third most productive university in Brazil

The university has published 16.998 articles between 2007 and 2011; USP (48.156) and Unicamp (17.130) lead the ranking in Brazil.

http://www.unesp.br/portal#!/eng

Unesp in numbers

ENVIRONMENTAL NANOTECHNOLOGY LAB

Size

Cities with Unesp: 24
Schools and Institutes: 34

Programs of studies

Undergraduate programs: 169
Research master degrees programs: 110
Doctorate degrees programs: 91

Students

Undergraduate: 35,284
Graduate: 12,633

Teaching staff

3,316 (95% with P.h.D.)

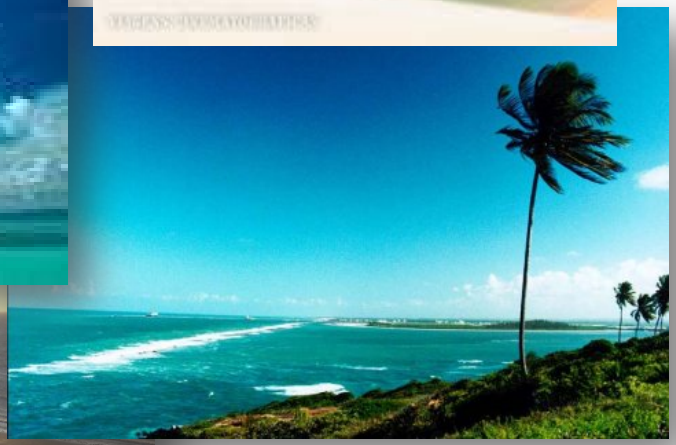
Localization

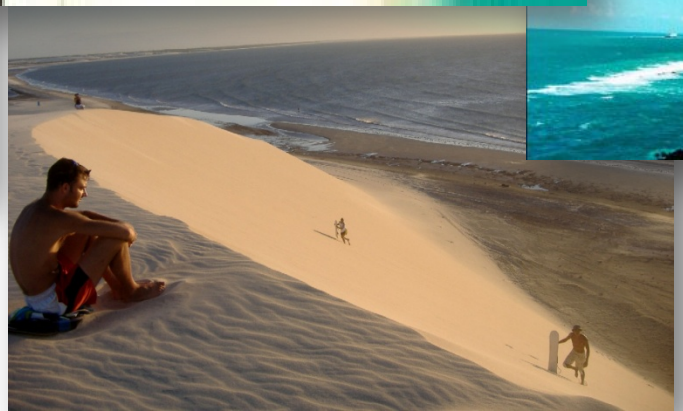
Population 600 000 inhabitants (2016)
Area de 456,0 km²
349,2 km² - Urban area

In Sorocaba there aren´t good soccer teams….

There aren´t famous samba schools

… neither beautiful beaches

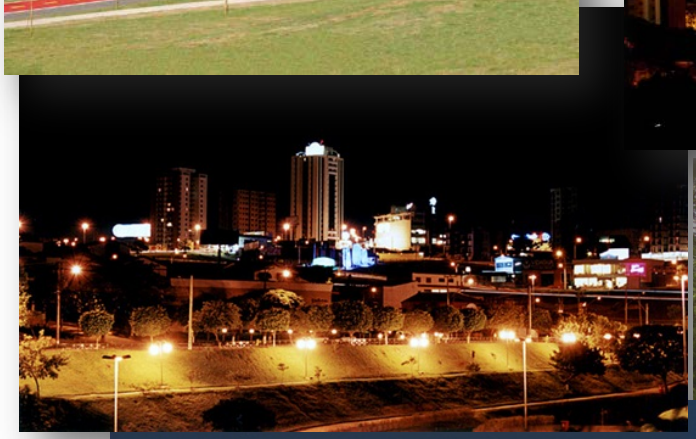




… neither beautiful falls

Sorocaba – a city to live and work!!!




Zoo


ZOOLÓGICO
ZOO QUINZINHO DE BARROS


Foto: Cátia Zela de Sá


Crânio de
Hipopótamo

Campus Sorocaba

ENVIRONMENTAL NANOTECHNOLOGY LAB

Facilities

ENVIRONMENTAL NANOTECHNOLOGY LAB

NTA

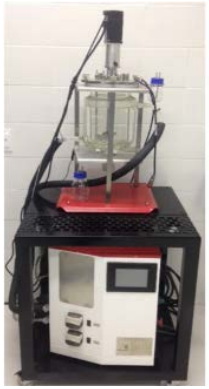
AFM

Particle size analyser

DSC

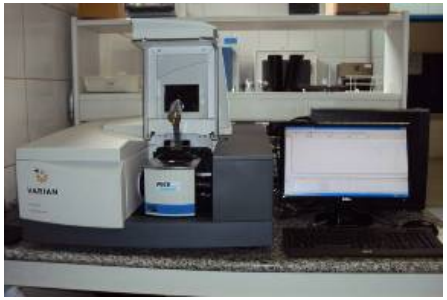
Chromatography

UV-Vis

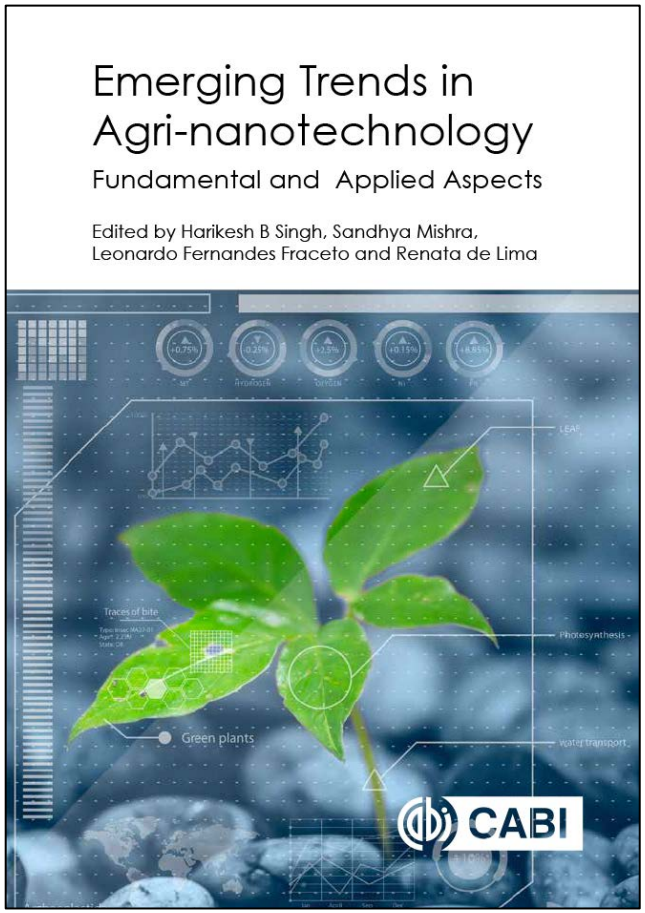


Bioreator

FTIR



Thank you!/Благодарю вас!/Blagodaryu vas!



- Contact:
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e-mail: leonardo.fraceto@unesp.br

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unesp

Paraquat case

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Journal of Hazardous Materials 278 (2014) 163–171

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Chitosan/tripolyphosphate nanoparticles loaded with paraquat herbicide: An environmentally safer alternative for weed control

Renato Grillo[a,b], Anderson E.S. Pereira[a,b], Caroline S. Nishisaka[c], Renata de Lima[c], Kathleen Oehlke[d], Ralf Greiner[d], Leonardo F. Fraceto[a,b,*]

Chemosphere 119 (2015) 608–619

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Review

Engineered nanoparticles and organic matter: A review of the state-of-the-art

Renato Grillo[a,b,*], André H. Rosa[a], Leonardo F. Fraceto[a,b,*]

Journal of Hazardous Materials 286 (2015) 562–572

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Chitosan nanoparticles loaded the herbicide paraquat: The influence of the aquatic humic substances on the colloidal stability and toxicity

Renato Grillo[a,b], Zaira Clemente[a,c], Jhones Luis de Oliveira[a], Estefânia Vangelie Ramos Campos[a,b], Victor C. Chalupe[c], Claudio M. Jonsson[c], Renata de Lima[d], Gabriela Sanches[d], Caroline S. Nishisaka[d], André H. Rosa[a], Kathleen Oehlke[e], Ralf Greiner[e], Leonardo F. Fraceto[a,b,*]

CS/TPP:Paraquat case

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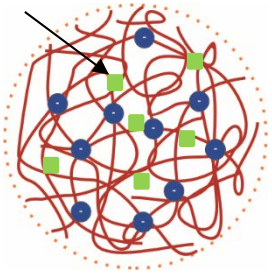
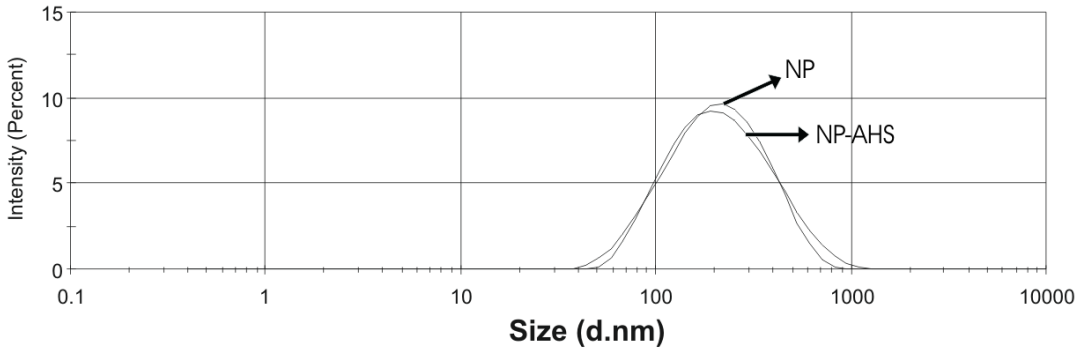
Paraquat

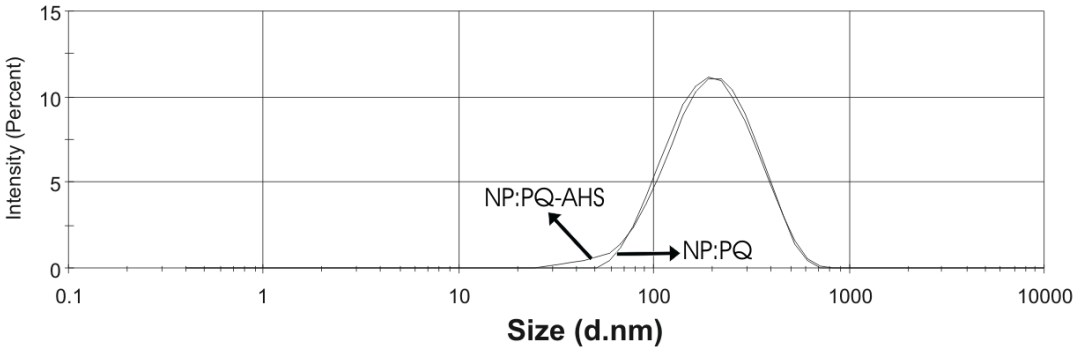


E.E.: 62.6 ± 0.7%

**** E.E. = Encapsulation Efficiency***



A)



B)

Size distributions of the CS/TPP nanoparticles, with and without AHS (20 mg L^{-1}), at pH 5: A) Nanoparticles without AHS (NP) and with AHS (NP-AHS); B) nanoparticles associated with PQ in the absence of AHS (NP:PQ) and with AHS (NP:PQ-AHS). The values represent the average of three experiments performed at 25 °C.

Paraquat case

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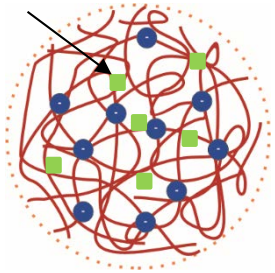
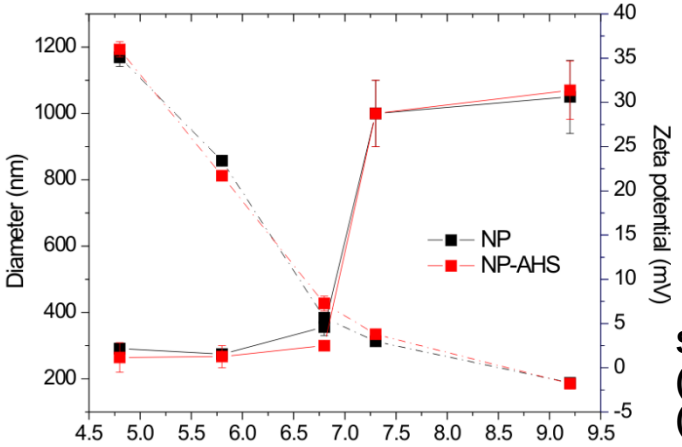
Paraquat

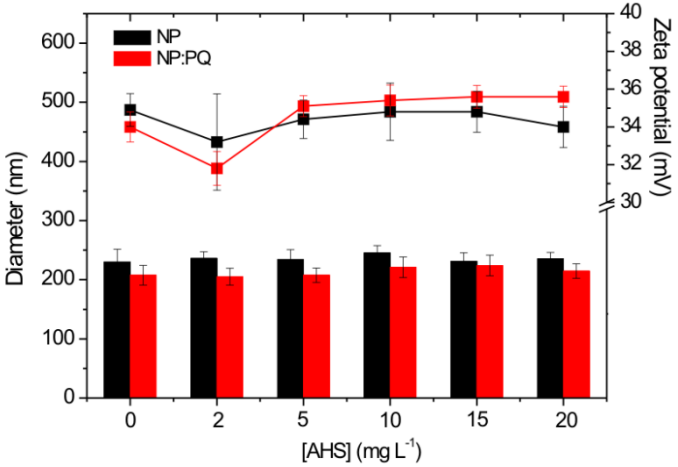


Aquatic Humic Substances (AHS)

Sorocabinha river (24º43'31,3''S e 47º35'42,6''W)



Stability of the nanoformulations with AHS (20 mg/L) by DLS: Hydrodynamic diameter (—) and zeta potential (---).



Values of the hydrodynamic diameter (columns) and zeta potential (lines) in different concentrations of AHC (0–20 mg/L, at pH 5.0).

Genotoxicity

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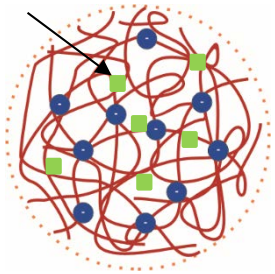
Paraquat



Aquatic Humic Substances (AHS)

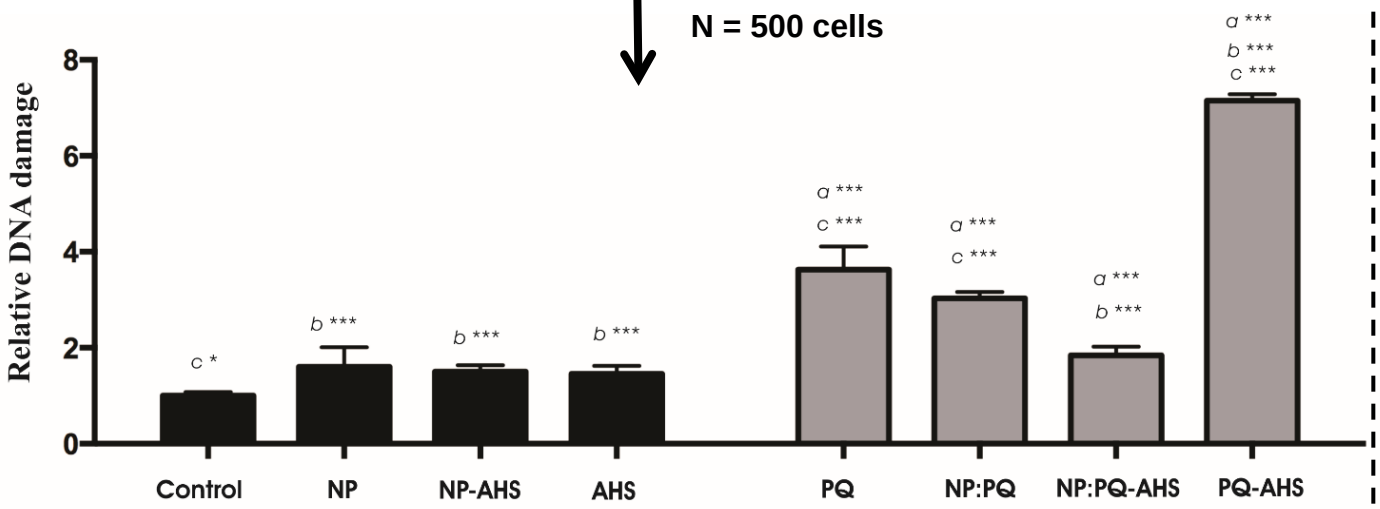
Competition between the herbicide molecules and potentially toxic substances complexed with the AHS.

GENOTOXICITY

[PQ] = 0.38 mg/L

[AHS] = 20 mg/L

N = 500 cells



Evaluation of chromosomal damage using the *Allium cepa* test with and without AHS.

Hypothesis…

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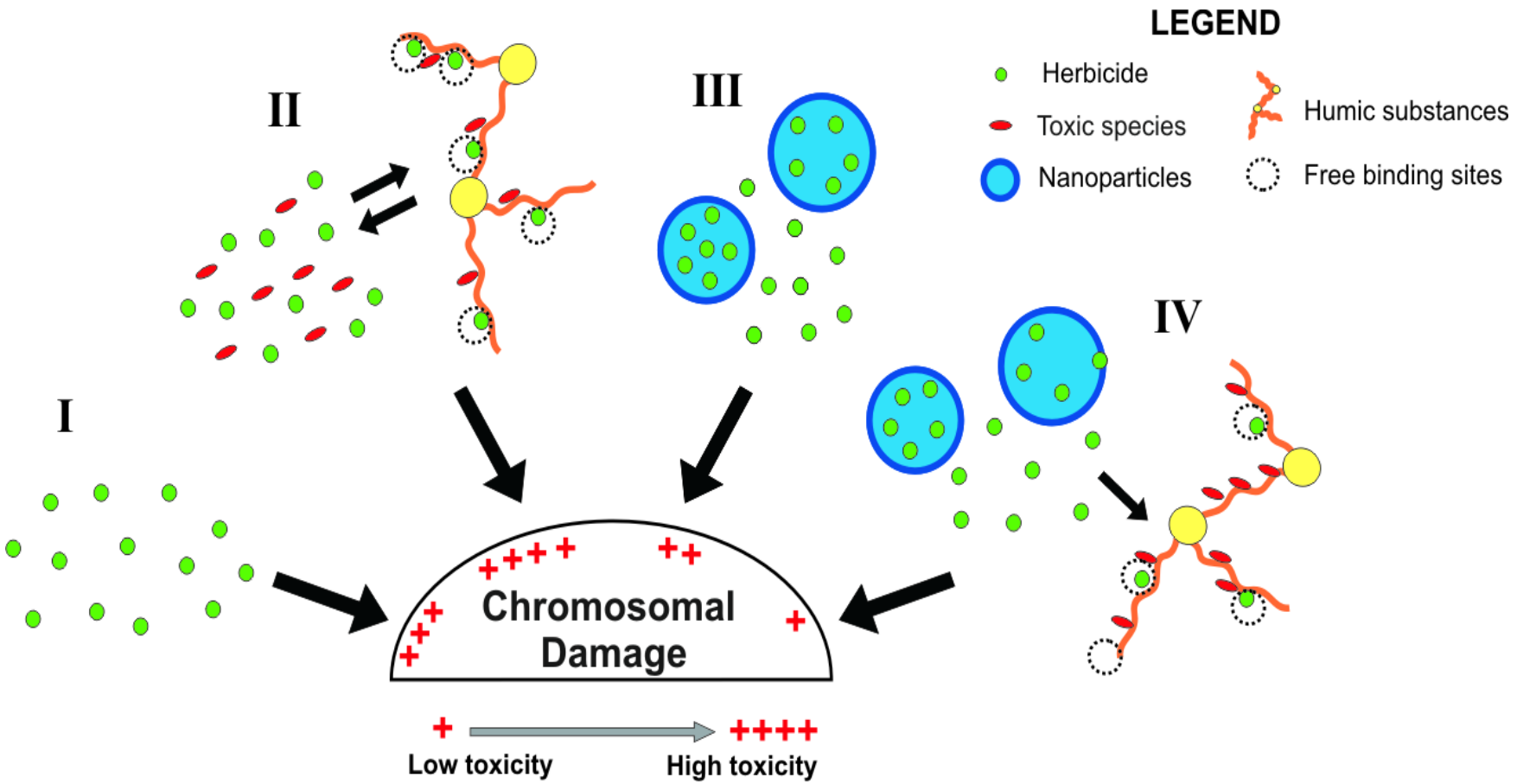

Schematic representation of the chromosomal damage observed for: I) free PQ, II) Paraquat with AHS (PQ-AHS); III) Paraquat combined with the NPs (NP:PQ) and IV) NPs with PQ and AHS (NP:PQ-AHS). Symbol (+) represent increased of the chromosomal damage to *Allium cepa* cells.