

Nano-pesticides and options for protecting farmworkers

Steve Suppan International Seminar (via video) Ministry of Labor: São Paulo, Brazil November 27, 2019

RAQUEL VON HOHENDORFF WILSON ENGELMANN

NANOTECNOLOGIAS **APLICADAS AOS** AGROQUÍMICOS NO BRASIL A Gestão dos Riscos a Partir do **Dialogo Entre as Fontes do Direito**

What we've learned about impacts, risks and toxicity since von Hohendorff/ Engelmann (2014)

- "Little is understood yet about nano-toxicity. The levels of nanoexposure are not known; the levels of exposure that could be harmful to human health are not known nor whether there is a safe limit of exposure. Furthermore, there are few studies about long term exposure to research the potential toxicity of these products." (p. 72)
- Unfortunately, this summary continues to be valid, **save for:**
- Bio-persistent nano-particles (NPs) can be measured and visualized as they move in the human body for up to 365 days
- The most hazardous NPs can be identified by means of screening nanoinformatic data bases of *in vivo* and *in vitro* experiments
- However, there is no agreement on nano-relevant risk assessment metrics for regulation and particularly for protection of workers



Overview: nano-pesticides and the occupational health of farmworkers

- Why nano-pesticides?
- Types of nano-pesticides, according to the report of the Brazilian Agribusiness Research Corporation (EMBRAPA)
- Brief U.S. nano-pesticides history: EPA permitting commercial use without published risk analysis
- Kocide®: EPA registered in 2015: label on use and EPA's revised Worker Protection Standard
- Controls to protect lab technicians from NP exposure: feasible to apply to farmworkers?
- "Safe by Design" (SbD) NPs: a future of nano without rules?

Nano in the Agri-tech revolution

https://www.nature.com/articles/s41565-019-0461-7

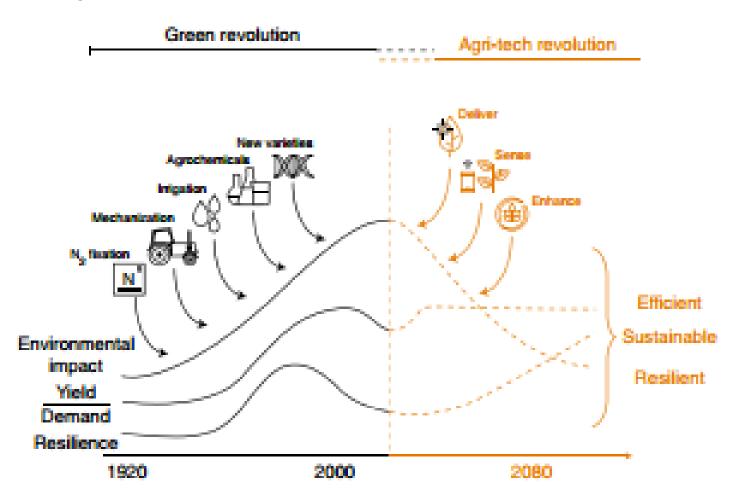
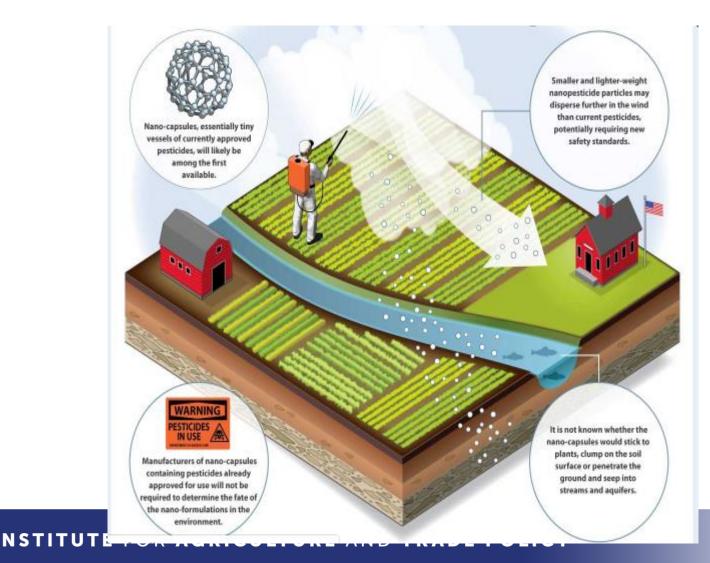


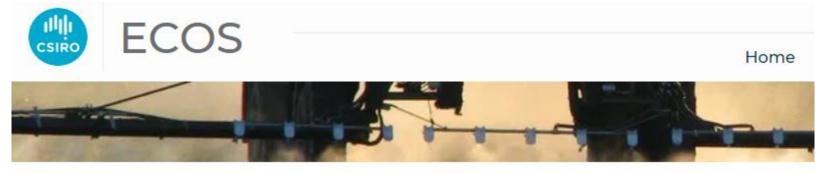


Fig. 1 | The green revolution and the new agri-tech revolution. INSTITUTE FOR AGRICULTURE AND TRADE POLICY

V. Gerwin: "Everything you need to know about nano-pesticides": *Modern Farmer*, 1/21/15



"Currently, there is little understanding of the risk associated with this emerging technology" Rai Kookana (2015) https://ecos.csiro.au/nanopesticides-a-promising-new-pesticide-solution/



A / 2015 / Issue 210 / Nanopesticides: a promising new pesticide solution?

Nanopesticides: a promising new pesticide solution?

By Virginia Tressider

August 4th, 2015



Kookana et al : Guiding Principles for Regulatory Evaluation of Environmental Risks (2014)

https://pubs.acs.org/doi/pdf/10.1021/jf500232f

Journal of Agricultural and Food Chemistry



Table 1. Potential Applications of Nanotechnology in the Pesticides Sector

function	how this can be achieved	current examples
enhanced apparent solubility	nano- and microemulsions	emulsion-based registered pesticides, Banner MAXX of Syngenta ⁶⁴
faster decomposition in soil and/or plant	nanocatalyst-conjugated ai in microcapsules	SDS-modified TiO ₂ /Ag conjugated with ai such as dimethomorph; ⁶⁵ imidacloprid and avermectin ⁶⁶
controlled release	nanocapsules, nanospheres	polymeric stabilized bifenthrin; ⁶⁷ nanocomposite 2,4-D; ⁶⁸ porous hollow Si- encaged validamycin ⁶⁹
targeted delivery	nanocapsules	nanoenapcsulated glyphosate or sulfonylurea herbicide ²
protection against premature degradation	nanocapsules with catalyst ai conjugate	TiO ₂ -M262 polymer metaflumizone; ⁷⁰ porous hollow Si-encaged validamycin ⁶⁹
enhanced uptake/efficacy	nano- and microemulsions, nanospheres	nanopermethrin; ⁷¹ nanosphere insecticides ⁷²
enhanced toxicity to target organism (lower dose)	nanodispersions; nanosuspensions	nanodispersed triclosan ⁷³
nanoparticle as ai	nanometals and nanoclays	registered Nano-Ag biocide; ⁷⁴ Nano-Si ^{75,76}



Absent from the analysis of nano-pesticides: impacts on worker health (2018)

https://www.researchgate.net/publication/324992564_A_critical_evaluation_of_nanopesticide s_and_nanofertilizers_against_their_conventional_analogues

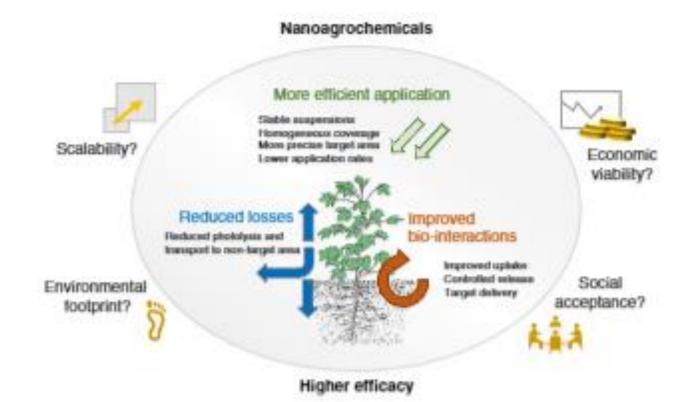


Fig. 1 | Key drivers for applying nanotechnology to improve the efficacy of agrochemicals. Associated socio-economic and environmental considerations that still need to be addressed are shown around the centre.

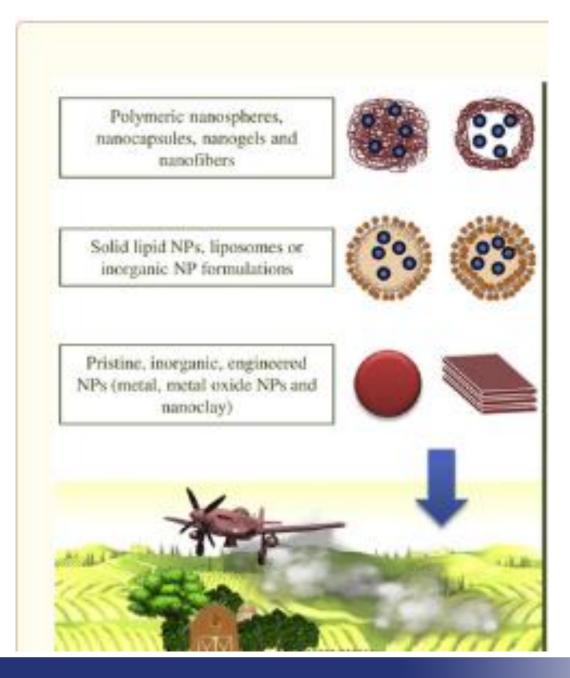


Nano-pesticides: types, properties, challenges

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6380358/

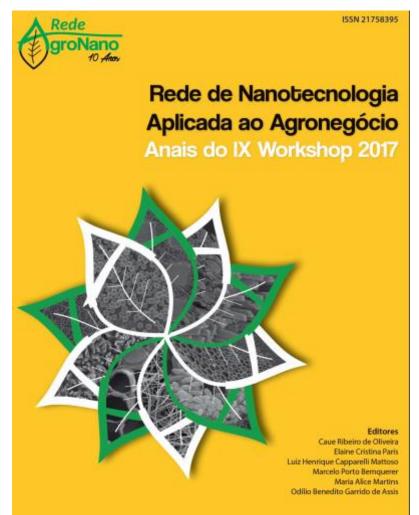
Nanopesticides	✓ Greater pesticide solubility,	✓ Biosafety of
✓ Nano-emulsions, -dispersions, -	mobility and durability;	nanopesticides;
spheres,- capsules, and -gels of	✓ Reduced amount of	✓ Toxicological
traditional pesticides;	ingredients via	profile;
✓ Solid lipid NPs, coated	targeted/controlled release;	interactions with
liposomes, or inorganic	✓ Reduced resistance and	co-formulants;
NPs associated with active	damage to nontarget organisms.	environmental
ingredients;		fate;
✓ Engineereed NPs, i.e. Ag-and TiO		✓ Long term
2-NPs.		effects on the
		environment and
		chronically
		exposed workers







Summaries of 170 studies; 4 on nanopesticides; none on health impacts







Most efficient NP form to control insecticide release to reduce harm to citrus plants without unintended effects?





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ESTUDOS PRELIMINARES APLICADOS AO NANOENCPSULAMENTO DE INSETICIDAS NEONICOTINÓIDES: TIAMETOXAM

(Márcia R. Assalin¹, Débora C. S.Dutra¹, Maria A. Rosa¹, Rafaela C.R.M. Duarte¹, Patrícia Donaire², Nelson Duran²

(¹ EMBRAPA Meio Ambiente, Rodovia Campinas Mogi-Mirim, Tanquinho Velho, CP. 69, CEP 13820-000, Jaguariúna, SP, Brazil.² Laboratório de Química Biológica, Instituto de Química, Universidade Estadual de Campinas, CP 6154, CEP 13083-970, Campinas, SP, Brazil) Márcia.assalin@embrapa.br

Classificação: Tecnologias de micro e nanoencapsulação de princípios ativos



Biogenic silica capsules to optimize rate of pesticide release for 3 levels of salinity, pH and temperature





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SÍLICA BIOGÊNICA COMO VEÍCULO NA LIBERAÇÃO CONTROLADA DE BIOCIDAS

Bruno D. Mattos^a, Tainise V. Lourençon^b, Washington L. E. Magalhães^c

^a PPG em Engenharia e Ciência dos Materiais (PIPE), Universidade Federal do Paraná (UFPR).
^b PPG em Engenharia Florestal (PPGEF), Universidade Federal do Paraná (UFPR).
^c Empresa Brasileira de Pesquisa Agropecuária - Embrapa Florestas

Classificação: Tecnologias de micro e nanoencapsulação de princípios ativos.



In vitro study: inhibit 3 pathogenic fungi with 3 Ag NP inoculation formulas: 13-75% inhibition compared to non-inoculated control plants





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NANOPARTÍCULAS DE PRATA BIOGÊNICAS PARA O CONTROLE DE FUNGOS FITOPATOGÊNICOS

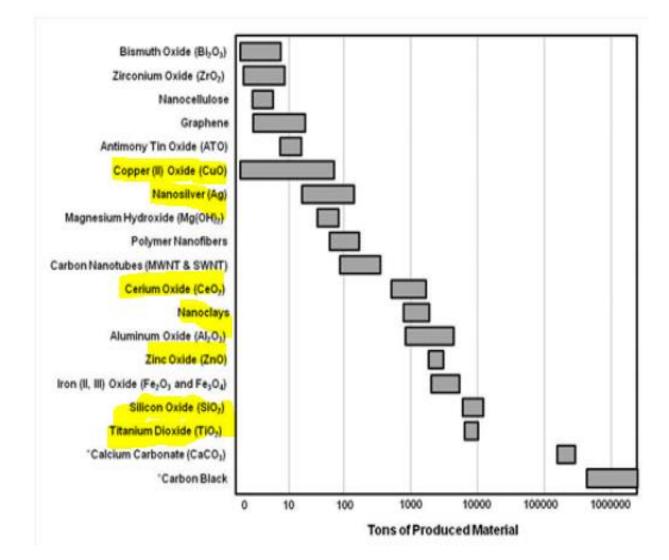
^{*}Mariana Guilger¹, Vitória A. N. Antunes¹, Leonardo Fernandes Fraceto², Renata Lima¹

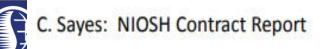
¹LABiToN – Laboratório de Avaliação de Bioatividade e Toxicologia de Nanomateriais, Universidade de Sorocaba (UNISO), Sorocaba, Brasil ²Departamento de Engenharia Ambiental, Universidade Estadual de São Paulo (UNESP), Sorocaba, Brasil *marianaguilger@gmail.com

Classificação: Novos materiais e processos em nanotecnologia e sua aplicação no agronegócio



Commonly Produced and Used NM



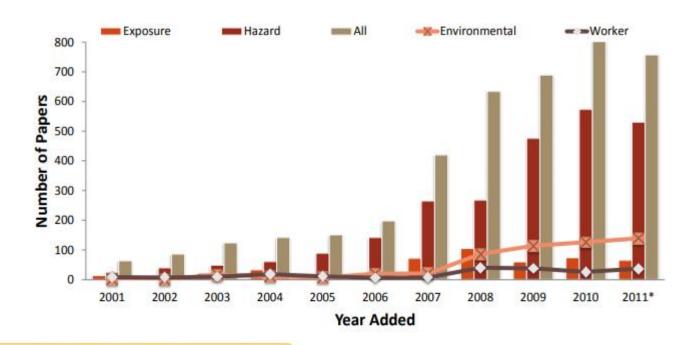


C. Geraci, NIOSH (2015)

https://www.nano.gov/sites/default/files/pub_resource/103_geraci_occu pational_exposure_review.pdf

What Does the Nano-EHS Research Tell Us?

Peer Reviewed Nano Environment, Health and Safety Journal Articles



http://icon.rice.edu/research.cfm



2015: EPA responds to a 2008 NGO petition to regulate nano-Ag as a nano-pesticide



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, DC 20460

OFFICE OF CHEMICAL SAFETY AND POLLUTION PREVENTION

March 19, 2015

The International Center for Technology Assessment 660 Pennsylvania Avenue, S.E., Suite 302 Washington, DC 20003

Subject: EPA Response to "Petition for Rulemaking Requesting EPA Regulate Nano-Silver Products as Pesticides"

Dear Petitioners:

Enclosed, please find the Agency's response to your petition, "Petition for Rulemaking Requesting EPA Regulate Nano-Silver Products as Pesticides," submitted on May 1, 2008. On November 19, 2008, EPA announced in the Federal Register its receipt of the ICTA petition and solicited public comments. The petition, supporting documents, and comments may be found in the public docket for this action at <u>www.regulations.gov</u> in Docket ID # <u>EPA-HQ-OPP-2008-0650</u>.



First permit to use nano Ag as a biocide for nonagricultural purposes (2011)

<u>https://news.bloombergenvironment.com/environment-and-energy/epa-announces-</u> <u>conditional-registration-for-antimicrobial-containing-nanosilver</u>

Environment & Energy Report

EPA Announces Conditional Registration For Antimicrobial Containing Nanosilver

Dec. 4, 2011, 11:00 PM

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Antimicrobial Pesticide Product With Nanosilver

Key Development: EPA issues conditional registration for antimicrobial pesticide product with nanosilver as an active ingredient.

Key Finding: Conditional use of AGS-20 will not pose unreasonable risk to children, environment, EPA finds.

What's Next: EPA is requiring further studies, including route-specific toxicity tests, during conditional registration period.



Anac ADDING IN	U.S. ENVIRONMENTAL PROTECTION AGENCY Office of Pesticide Programs Antimicrobials Division (7510P) 1200 Pennsylvania Avenue NW Washington, D.C. 20460	EPA Reg. Number: 85249-2	Date of Issuance: December 2011
	wasnington, D.C. 20460	Term of Issuance:	
Registrat	NOTICE OF PESTICIDE: Registration Reregistration	Name of Pesti HeiQ AGS-2	cide Product:
(under FIFRA, a	s amended)		
Name and Address HeiQ Materials Zürcherstrasse CH-5330 Bad Switzerland	42	and he	
	beling differing in substance from that accepted in connection with this regist prior to use of the label in commerce. In any correspondence on this produ		





Registration Decision for NSPW-L30SS (previously referred to as "Nanosilva")

A Materials Preservative for Use in Textiles and Plastics

Approved by:

Jack Housenger, Director Office of Pesticide Programs

Date: 5/15/15

Suing EPA for permitting nano-AG use without nano-relevant risk assessment



Suing EPA for failure to regulate nano-pesticides

Apr 2, 2015 by Dr. Steve Suppan



2017: a court rules EPA did not justify its registration of Nanosilva

https://product-liability.weil.com/consumer-products/court-finds-epa-lacked-substantialevidence-to-register-nanosilver-based-pesticide/



HOME WEIL'S PRODUCTS TEAM CONTACT

Court finds EPA lacked "substantial evidence" to register nanosilver-based pesticide

CAROLYN R. DAVIS on JULY 19, 2017

Posted in CONSUMER PRODUCTS

2015: EPA registers a nano-pesticide for organic horticulture, grains and soy

https://www3.epa.gov/pesticides/chem_search/ppls/091411-00002-20150507.pdf



NOTIFICATION

91411-2

The applicant has certified that no changes, other than those reported to the Agency have been made to the labeling. The Agency acknowledges this notification by letter dated:

05/07/2015

Dry Flowable	
Active Ingredients	
Copper Hydroxide* (CAS No. 20427-59-2)	
Inert Ingredients	

By Weight 46.1% 53.9% TOTAL 100.0%

EPA Reg. No.	91411-2	
Nonrefillable	Container	
OR		
Refillable Container		

(* Metallic Copper Equivalent 30%)

Kocide[®]3000

fungicide/bactericide

Net:

Net:

EPA Est. No.352-TX-003

EPA's conditions for use of Dupont [™]'s Kocide[®] 3000 described in a 19 page label

- For those who mix Kocide® with water or apply it: Personal Protection Equipment (PPE) of long-sleeved shirt, pants, impermeable gloves, shoes and socks
- Comply with EPA Worker Protection Standard
- Users are liable for all damages for use of Kocide®
- Can be applied on the ground or from an airplane in different concentrations
- Warning: stop using Kocide[®] when plants in greenhouses show signs of phyto-toxicity
- (No corresponding warning for horticulture workers in greenhouses)



Simonin et al (2018): first published environmental risk assessment of Kocide®

https://www.frontiersin.org/articles/10.3389/fmicb.2018.01769/full

- Active ingredient: nanoscale Cu(OH₂)
- Test field: "mesocosm" (precision greenhouse)
- Kocide[®] applied to 7 plants in soil with "ambient" (existing), low and high degrees of fertilization
- Soil and plant test at 15 days, 10 weeks and one year
- Results: no negative impact on plants or to plant-microorganism associations
- Risks to soil fertility (e.g. capacity to fix N, micro-organism biomass), especially under the low fertilization characteristic of organic agriculture for which Kocide® is registered
- Future research: environmental impacts of repeated applications of Kocide®



In vitro study: cellular toxicity in onions of Ag and Si NPs compared to trifuralin toxicity in pesticides





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CITOTOXICIDADE CAUSADA POR NANOMATERIAIS: AVALIAÇÃO DO MICRONÚCLEO

Anny Manrich1*, Silviane Zanni Hubinger1, Elaine Cristina Paris1

¹ Embrapa Instrumentação, Rua XV de Novembro 1452, 13560-970, São Carlos, SP *anny.manrich@gmail.com

Classificação: Cenários e avaliação dos riscos ambientais e sociais dos nanocompostos



Review of nano-pesticide studies: almost without data useful for occupational health protection <u>https://oem.bmj.com/content/75/Suppl_2/A470.3</u>

- Internet survey of scientific literature (2018)
- Nearly all studies focus on technical benefits (e.g. less mass of Active Ingredient applied)
- Very few *in vitro* studies comparing pesticide and nano-pesticide toxicity
- No *in vivo* studies comparing pesticide and nanopesticide toxicity
- Most probable vector of human health risk: dermal exposure during the mixing of the nano-pesticide



2006 EPA guidance to protect agriculture workers

https://www.epa.gov/sites/production/files/2015-

o6/documents/protectyourselffrompesticidesspanish_735_b_o6_oo1.pdf

United States Environmental Protection Agency Office of Prevention Pesticides, and Toxic Substances (H7506C)

EPA 735-B-06-001 Revised June 2006 (Spanish)



Protect Yourself from Pesticides– Guide for Agricultural Workers (Spanish)

Protéjase de los Pesticidas – Guía para los Trabajadores Agrícolas



2018: Worker Protection Standard enters into force: 146 pages for compliance by employers



How to Comply with the 2015 Revised Worker Protection Standard For Agricultural Pesticides

What Owners and Employers Need To Know



THUTE FOR AGRICULIONE AND TRADE FULCT

U.S. States implement EPA Worker Protection Standard, e.g. a Colorado poster

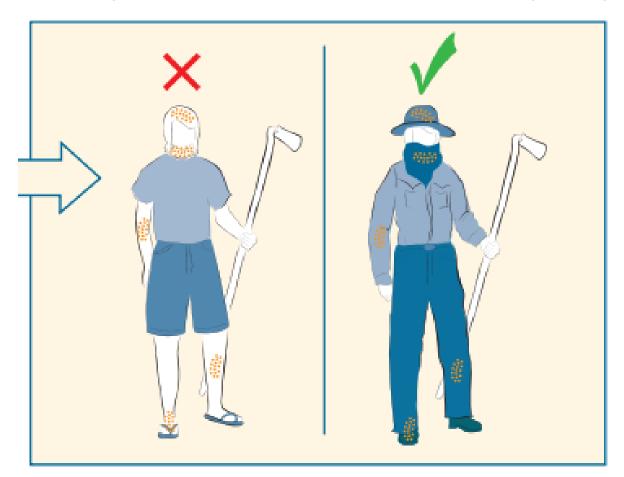


Evite que los pesticidas hagan contacto con su piel o entren en su cuerpo. Los pesticidas pueden estar en muchos lugares. Pueden estar sobre las plantas, dentro de las plantas, en el suelo y en el agua de riego. Los pesticidas pueden ser llevados por el viento desde aplicaciones cercanas. También pueden estar en tractores y otras



Personal Protection Equipment (PPE) in Colorado

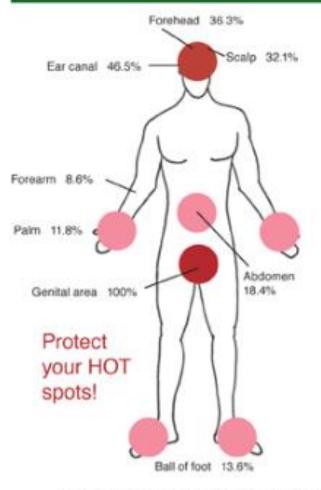
<u>http://cepep.wptest.agsci.colostate.edu/wp-</u> <u>content/uploads/sites/35/2016/06/PERC_CP_11x17_spanish.pdf</u>



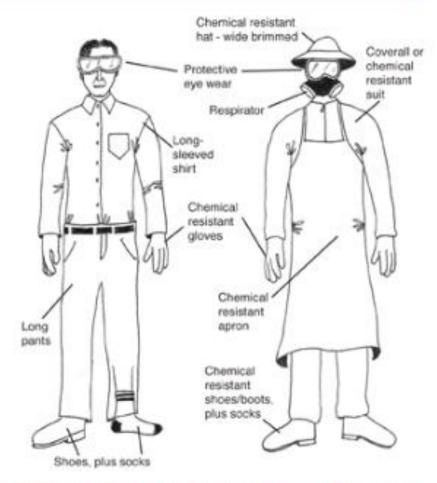
Proteja su cuerpo de los residuos de pesticidas. Use camisas de manga larga y pantalones largos cuando trabaje. Además use zapatos, calcetines y un sombrero o pañuelo.



Personal Protective Equipment (P.P.E.)



Percents indicate relative amount of absorption of pesticide over a 24-hour period. (Feldman and Maibach. 1974. Percutaneous penetration of some pesticides and herbicides in man. *Toxicology and Applied Pharmacology* 28, pp. 399–404).



P.P.E. must be washed and dried after each day's use and stored away from chemicals. Change gloves and respirators as per manufacturers' specifications.

Even in Syngenta's experimental farm in Hawaii

https://legalnewsline.com/stories/511065024-epa-targets-syngenta-seeds-seeks-4-<u>8-million-for-alleged-worker-protection-law-violations</u>

EPA targets Syngenta Seeds, seeks \$4.8 million for alleged worker protection law violations

By Mark landolo | Jan 4, 2017





Adapt NIOSH research to protect farmworkers

https://www.cdc.gov/niosh/docs/2019-116/pdfs/2019-116.pdf



Figure 3. The critical research areas of the NIOSH Nanotechnology Research Center (NTRC).

Steps towards protecting farmworkers

- Develop PPE adequate to prevent exposure to nano-pesticides, e.g. much better HEPA masks
- Monitor worker exposure to NPs with appropriate instruments, e.g. on instruments on PPE
- Take biological samples in the field or greenhouse
- Analyze the samples per initial route of exposure in the working environment of nano-pesticide use
- Use sampling and monitoring data for "Safe by Design" NPs in nano-pesticides and PPE design

C. Sayes, "Exposure in Biological Systems: State of the Science" (2015): adaptable to farmworkers?

The most useful monitoring data is when personal, area, and biological samples are collected within the same system Screen areas Collect samples at Analyze biological source and personal fluids and processes Consider the Probing for changes in space biomarker levels particular Including chemical characteristics of and physical Attention to a facility properties of the immediate biological nanomaterial response Area Personal **Biological REFERENCES:** UC Santa Barbara (http://www.cns.ucsb.edu) SafeNano (http://www.safenano.org/knowledgebase/guidance/safehandling/) NanoSafe, Inc. (http://www.nanosafeinc.com)

NIOSH (http://www.cdc.gov/niosh/topics/nanotech/)



Detection and Measurement of Nanoparticles - PERSONAL

Protective Equipment

- Dermal exposure reduction
 - Gloves
 - Lab coats
 - Based on conventional IH
- Inhalation exposure reduction
 - Respirators, dust masks
 - HEPA filtration
- Ocular exposure reduction
 - No contact lens
 - Safety glasses or goggles

Monitoring

- Personal samplers
- Gravimetric measuring (filter-based)
- Photometric measuring

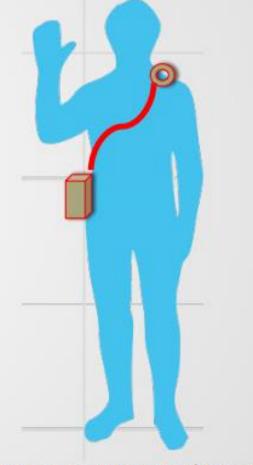


Image courtesy Wikimedia



EU project to reduce NP risk before NPs are incorporated into products



Projects Working Groups Task Forces Cooperation Publications & Outputs Activities News & Events NSC Meetings

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Horizon 2020 Projects	
Ongoing Projects:	
ACEnano	
Calibrate	
CERASAFE	
EC4SafeNano	
GRACIOUS	
Hisents	

Home

NanoREG II

NanoREG II: Development and implementation of Grouping and Safe-by-Design approaches within regulatory frameworks

Coordinator: Institut National de l'Environnement Industriel et des Risques (INERIS)

Participants:

- EUROPEAN VIRTUAL INSTITUTE FOR INTEGRATED RISK MANAGEMENT EU VRI EWIV (Germany)
- NANOTECHNOLOGY INDUSTRIES ASSOCIATION (Belgium)

With or without nano rules: a hierarchy of controls with SdB NPs in first place (P. Schulte, NIOSH) https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5923569/

Journal List > Nanomaterials (Basel) > v.8(4); 2018 Apr > PMC5923569

Nanomateria



Nanomaterials (Basel). 2018 Apr; 8(4): 239. Published online 2018 Apr 14. doi: <u>10.3390/nano8040239</u> PMCID: PMC5923569 PMID: 29661997

Implementation of Safe-by-Design for Nanomaterial Development and Safe Innovation: Why We Need a Comprehensive Approach

Annette Kraegeloh,¹ Blanca Suarez-Merino,² Teun Sluijters,³ and Christian Micheletti^{2,*}

Author information + Article notes + Copyright and License information Disclaimer



Nano-informatics: crucial for converting data into SbD NPs

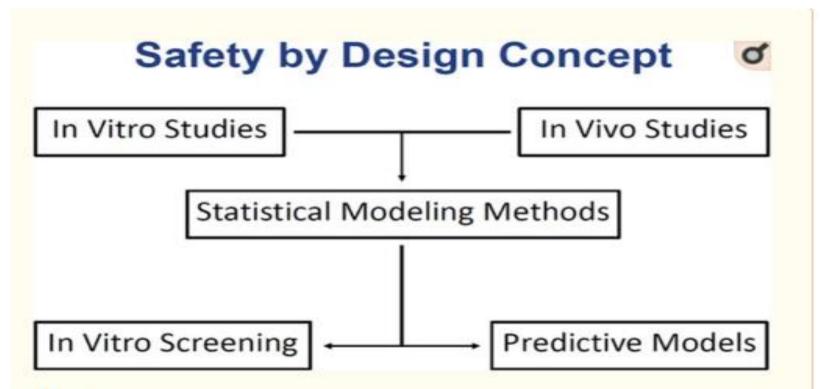


Figure 3

The use of in-vitro and in-vivo data to develop predictive models that support characterization and biological activity prediction



Table 1

Safe-by-Design (SbD) strategies described in scientific publications (2011-2018).

SbD Strategy	Measure
	NanoParticle (NP) doping
Design out hazard (direct and indirect effects of nanomaterials)	Surface passivation
	NP coating
	Reduction of photo-catalytic efficiency
	Formation of composites
	Surface functionalisation
Reduce release	Adaptation of the processing
	Selection of nanofiller
Reduce bio-persistence	Carbon NanoTubes (CNT) Doping
Testing strategies for safety evaluation	High throughput screening, alternative testing
Testing strategies for safety evaluation	strategies and biological mechanisms
Material characterisation	
Identification of risk hotspots for	End of life cycle: thermal decomposition
potential SbD approaches	Life cycle assessment
Pilot plant development	Risk mitigation



Safe by Design cannot reduce nano-pesticide risks if deregulation to protect agribusiness increases pesticide risks

<u>https://thehill.com/policy/energy-environment/467357-trump-administration-rule-to-shrink-exclusion-boundaries-near</u>



Trump administration rule to shrink exclusion boundaries near pesticide applications

BY MIRANDA GREEN - 10/24/19 04:33 PM EDT

46 COMMENTS



Conclusions and questions 1

- State of the science for nano-pesticides: environmental health (incipient); human health (non-existent)
- How to analyze nano-pesticides risk in the field conditions of its use?
- According to the EU, the OECD standards on biocides are inadequate for risk analysis of nano-biocides (industrial and agricultural uses)
- Nevertheless, the EPA allows use of nano-pesticides based on data submitted by the applicants as confidential business information



Conclusions and questions 2

- Consensus: nano metal (e.g. Ag, Cu) and metal oxides (e.g. TiO₂) are most hazardous NPs, due to their biopersistence and other properties
- Which types of nano-pesticides pose the greatest risks?
- Does nano-encapsulation reduce AI risks?
- Can SbD techniques reduce exposure to NPs to reduce risks for farm workers using nano-pesticides?
- PPE for use with nano-pesticides does not yet exist
- Can PPE for lab technicians be adapted to protect farm workers?



Government response to non-nano means to reduce the volume of pesticide use



TAKE ACTION THE PESTICIDE PROBLEM

A Brazilian agroecology training center is a target for eviction



