Life Cycle Assessment of nanoTiO_2 and its applications

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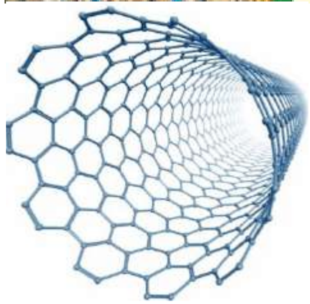
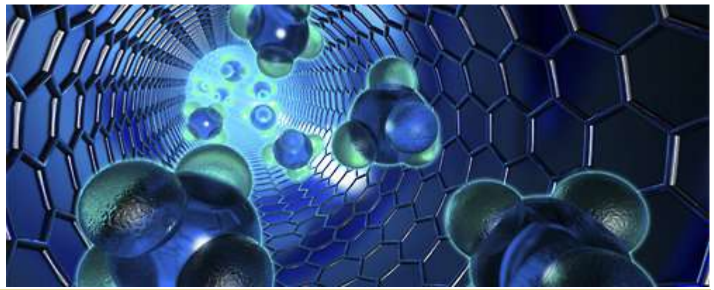
This presentation concerns the research activities of Martina Pini's PhD

Doctorate School in Industrial Innovation Engineering



Summary

1. Overview of research activities
2. Determination of potential damage of nanoTiO_2
3. Determination of indoor and outdoor benefits of nanoTiO_2
4. LCA case studies
5. Conclusions

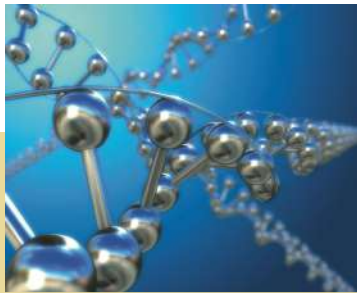


Overview of research activities

www.aracne.emr.it

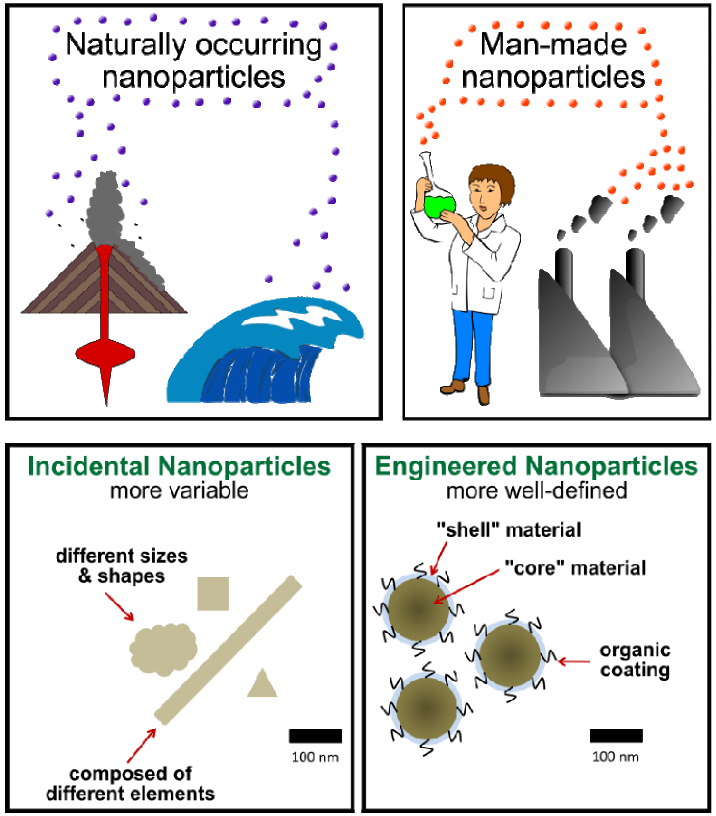
- ARACNE Italian project
  - 3 companies of Emilia-Romagna region
  - University of Modena and Reggio Emilia
  - University of Bologna

- Aim: study new and eco-friendly building materials with higher technological properties obtained by the addition of specific nanomaterials.



Nanoparticles and ENPs

- “nanoparticles”: materials with all three dimension between 1 and 200 nm in size.
- Commonly nanomaterials are based on engineered nanoparticles (ENPs).
- ENPs is referred to manufactured materials:
  1. Metal oxides (***TiO_2***, ZnO ect.)
  2. Carbon based products (carbon nanotubes)
  3. Metals (gold and silver NPs)
  4. Quantum dots (semiconductor nanocrystal)
  5. Dendrimes (multifunctional polymers)



Properties & Applications of nanoTiO_2

nanoTiO_2+Light
Photocatalysis
Superhydrophilicity

Self-cleaning
- Building and Road materials
- Electrical & Electronic Equipment

Anti-fogging
- Building and Road materials
- Vehicles
- Electrical & Electronic Equipment
- Paint

Air cleaning
- Indoor air cleaners
- Outdoor air purifiers

Water purification
- Drinking water

Self-sterilizing
- Hospital
- Clean rooms

Cosmetic and skin care products

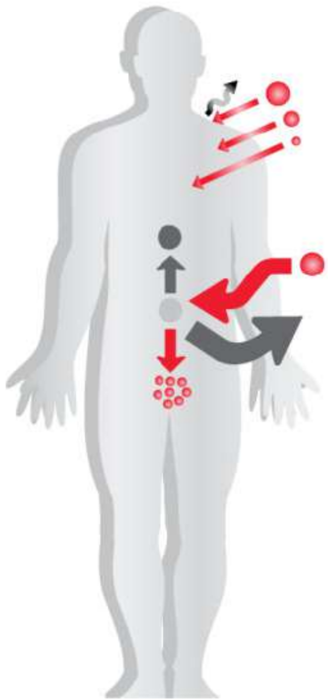
Determination of potential damage of nanoTiO_2

Nanotoxicity assessment

- Uncertainties and knowledge gaps on behavior and toxicity of nanoparticles.

We cannot remain silent!!

- The LCA methodology can help to determine the potential impacts of nanoproducts and nanomaterials on human health and enviroment.



Nanotoxicity assessment

- Damage caused by nanoTiO_2 emissions:

Human Health (HH)	*1. released in air (outdoor)*
	2. inhaled by workers (indoor)
	3. released in freshwater ecosystem
Aquatic Organism (AO)	*4. released in freshwater ecosystem*

Damage to HH caused by nanoTiO_2 emissions

1. *released in air (outdoor)*
2. *inhaled by workers (indoor)*

References		
NIOSH *National Institute for Occupational Safety and Health*	Occupational exposure limits for ultrafine TiO_2 (primary particles diameter < 100 nm)	**0.3 mg/m^3**
	Reducing the risk of developing lung cancer with concentration level of 0.3 mg/m^3	< 1/1000
IARC *International Agency for Research on Cancer*	TiO_2 review→ sufficient evidence of carcinogenicity in experimental animals and inadequate evidence of carcinogenicity in humans	Group 2B "**possibly carcinogenic to humans**"

Assumptions for the production step

Emissions released into the production room during the production step:

1%

99% of emissions are captured by the vacuum system

1% of emissions are released directly into the production room

99.97% is captured by HEPA filter.

0.03% is directly released in air

A fraction of emissions is inhaled by the worker, the rest is released outdoor by opening windows.

1. Damage to HH caused by nanoTiO_2 emissions released in air

Calculation of the damage caused by carcinogenic substance by Eco-indicator 99 method:

1- Fate analysis

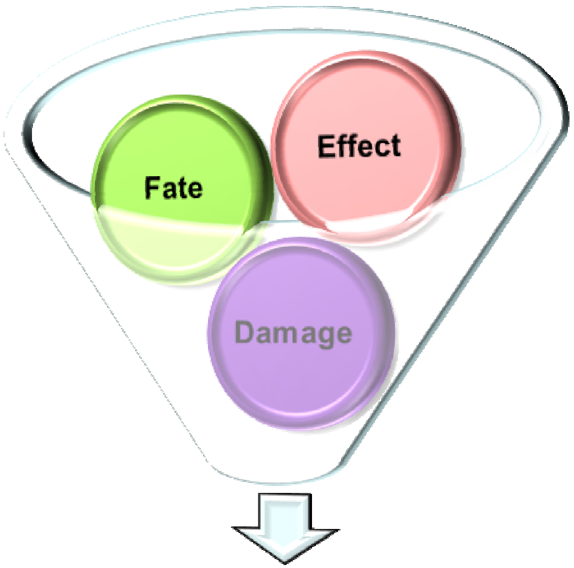
ASSUMPTION: nanoTiO_2 fate factor= **PM 2.5 μm Fate Factor (F)**= 1.70E-5 $m^2 yr/m^3$

2- Effect analysis

Unit risk factor (UR): 9.44E-5 persons/m^2

Effect factor (E): **UR*PD**= 4.49E-13 cases/$\mu g/m^3/yr$*persons/m^2

Incidence factor (I): **E*F**= 7.633 E-9 cases/$kg_{nanoTiO_2}$



3- Damage analysis

YLL (*years of life lost*)= 40 years

Damage assessment factor of ***Carcinogens*** category of IMPACT 2002+ method: 2.8E-6 DALY/kg_{C2H3Cl}

Characterization factor: 3.052E-7DALY/kg/2.8E-6DALY/kg=**0.109kg_{C2H3Cl}/kg $_{nanoTiO_2}$**

1. Damage to HH caused by nanoTiO_2 emissions released in air

Modification of IMPACT 2002+ method

In *Carcinogens* impact category:

New substance: *Particulates, <100 nm, in air*

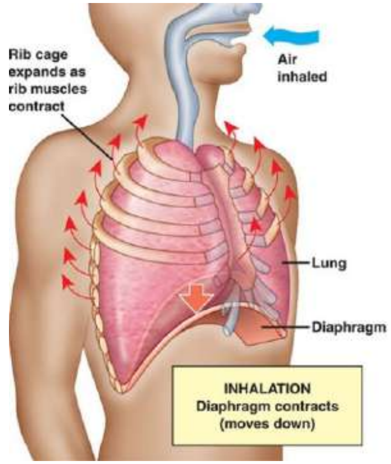
Characterization factor: 0.109 $kg_{C2H3Cl}/kg_{nanoTiO_2}$

Data input

Quantity of nanoTiO_2 emissions release in air.

2. Damage to HH caused by nanoTiO_2 emissions inhaled by workers

Concentration limit of indoor emissions in the production room:
275.725g/h/1200m^3= 0.227mg/m^3/h



Probability to contract the lung cancer:
1/1000*0.227mg/m^3/0.3mg/m^3= 7.56E-4

Damage assessment factor:
5workers*40YLL/workers*7.56E-4/0.0275725kg/h= **5.56 DALY/kg/h**

2. Damage to HH caused by nanoTiO_2 emissions inhaled by workers

Modification of IMPACT 2002+ method

New substance: *Particulates, <100 nm indoor*

New impact category: *Carcinogens indoor* [kg]

Characterization factor: 1kg/kg

New damage category: *Carcinogens indoor* [DALY]

Damage assessment factor: 5.56 DALY/kg

Data input

Quantity of nanoTiO_2 emissions inhaled by workers

3. Damage to HH caused by nanoTiO_2 emissions released in freshwater ecosystem

ASSUMPTIONS

- Emissions released during the purification of nanocontaminated water: 1kg/yr
- Water bodies volume of Reggio Emilia province: 9E6m^3
- Nanoparticles Concentration (C): 1.111E-7 kg/m^3
- Emissions per m^2 (E): 1E-4 kg/(m2*yr)
- The limit concentration it has been assumed of 8.33μg/L

Kumar A., et al., "Exposures to TiO_2 and Ag Nanoparticles: What are Human Health Risks?", Science and Society, 9(2), 2011.

3. Damage to HH caused by nanoTiO_2 emissions released in freshwater ecosystem

Calculation of the damage caused by carcinogenic substance by Eco-indicator 99 method:

1- Fate analysis:

Fate Factor (F): C/E= 1.111E-3 m^2*yr/m^3

2- Effect analysis:

Unit risk factor (UR): 2.34E-4 persons/m^2

Effect factor (E): **UR*PD**= 4.02E-13 cases/μg/m^3/(m^2*yr)*pers

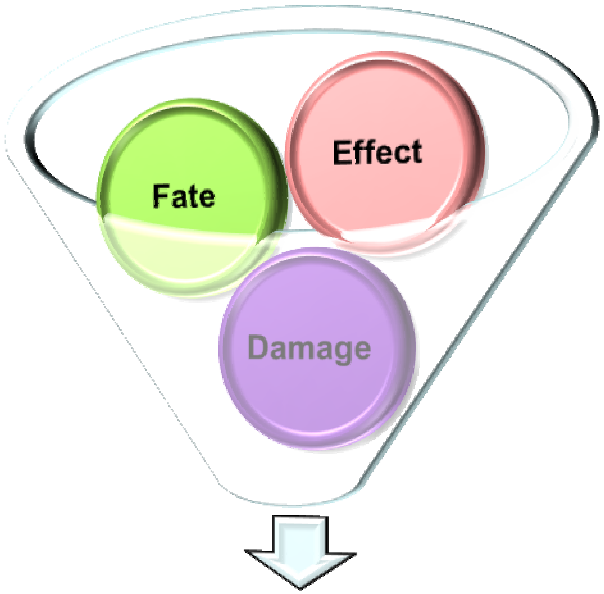
Incidence factor (I): **E*F**= 4.464E-7cases/$kg_{nanoTiO_2}$

3- Damage analysis:

YLL (*years of life lost*)= 30 years, YLD (*years lived disability*)= 2 years.

Probability to cure cancer: 50%

Damage Factor=16 DALY/case



Damage assessment factor: **I*D**=4.46E-7cases/kg*16DALY/case= **7.14E-6DALY/kg**

3. Damage to HH caused by nanoTiO_2 emissions released in freshwater ecosystem

Modification of IMPACT 2002+ method

New substance: *NanoTiO_2 Human toxicity*, in water

New impact category: *NanoTiO_2 carcinogens in water* [kg]

Characterization factor: 1kg/kg

New damage category: *NanoTiO_2 carcinogens in water* [DALY]

Damage assessment factor: 7.14E-6 DALY/kg

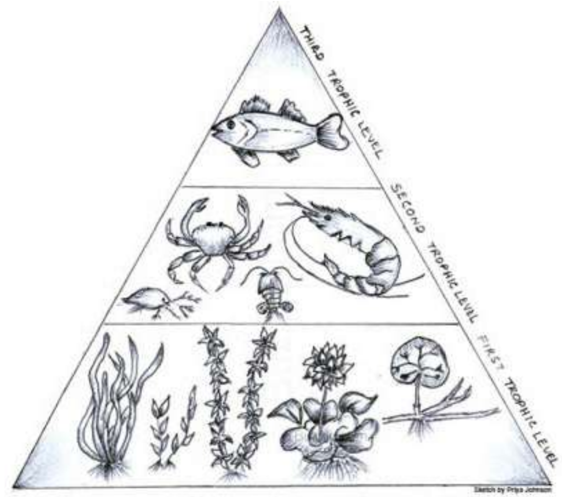
Data input

Quantity of nanoTiO_2 emissions which are not captured by filter.

4. Damage to AO caused by nanoTiO_2 emissions released in freshwater ecosystem

Reference

Salieri B., Olsen S.I., Righi S., *How to calculate the characterisation factor for nanoparticle? A case study on n–TiO_2*, Rete Italiana LCA, Milano 2013.



4. Damage to AO caused by nanoTiO_2 emissions released in freshwater ecosystem

Modification of IMPACT 2002+ method

New substance: *Particulates,<100nm, in water*

New impact category: *Nano ecotoxicity in freshwater* [kg]

Characterization factor: 1kg_{C2H3Cl}/kg

New damage category: *Nano ecotoxicity in freshwater* [PAF*day*m^3/kg]

Damage assessment factor: 0.28 PAF*day*m^3/kg

Data input

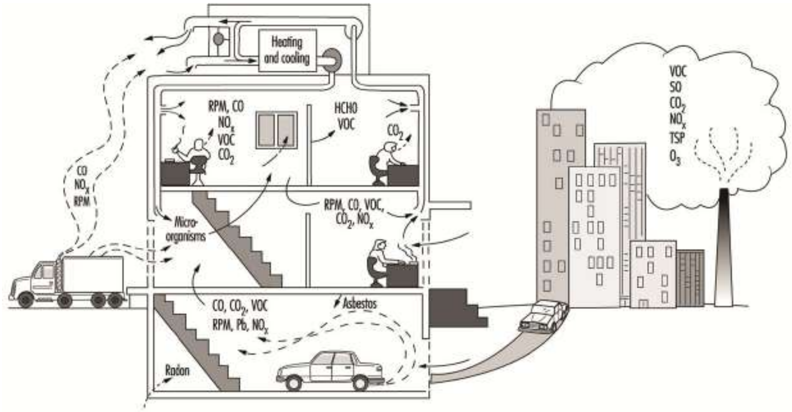
Quantity of nanoTiO_2 emissions release in water (not captured by filter).

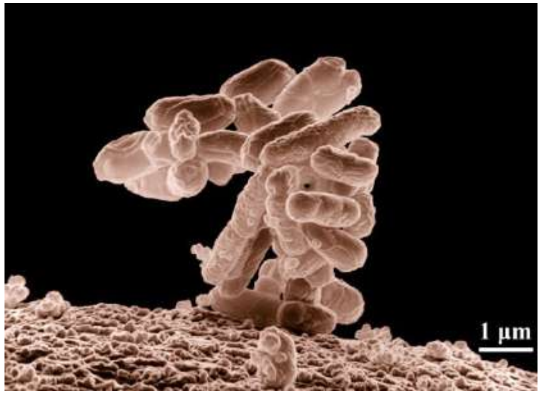
Determination of indoor and outdoor benefits of nanoTiO_2

Benefits indoor of nanoTiO_2

- Reduction of *NO_2 emissions* in air

Reference: *Italian environmental protection agency* study (ARPA Lombardia, 2004).
Results: reduction of 37% NO_2 indoor emissions.





- Evaluating of the survival ratio of *Escherichia Coli* exposed to a nanoTiO_2

It has been assessed in agreement with the results of Caballero et al., 2009. The survival ratio of E. Coli is 16.83%.

Benefits outdoor of nanoTiO_2

- Reduction of *NO emissions* in air:

  4.01 mg h^{-1} m^{-2} of NO removal

  Poon CS et al., Construction and Building Materials 2006;21(8):1746–53

- Reduction of VOC (*Toluene) emissions* in air:

  100 mg h^{-1} m^{-2} of Toluene removal

  Demeestere et al., Building and Environment 2008;43(4):406–14

LCA case studies

1. nanoTiO_2 suspension obtained by a liquid-phase process

   Collaboration: Colorobbia Italia S.p.A.

Life Cycle Assessment of nanoTiO_2 coatings

1. nanoTiO_2-polyurea resin applied on an aluminium panel
   Collaborations: Industrial Mechanical Plant research group and SRS S.p.A. company.
2. nanoTiO_2 coated self-cleaning float glass.
   Collaboration: Department of Engineering "Enzo Ferrari", Modena.
3. nanoTiO_2-glaze applied on an steel panel.
   Collaborations: Industrial and Mechanical Plant research group (DISMI) and Smaltiflex S.p.A. company.

1. LCA of nanoTiO_2 suspension

1. LCA of nanoTiO_2 suspension

Composition of nanoTiO_2 suspension	
Titanium isopropoxide (TIP)	23.22%
Water (H_2O)	73.40%
Nitric Acid (HNO_3) 63%	2.38%
Polyethylene glycol (PEG)	1%
Total	100%
Recycled Isopropanol ***Coproduct***	**12%**
Yield	88%
Products	
nanoTiO_2 + H_2O + HNO_3 + PEG	**85.71%**
H_2O deionized ***Coproduct***	**14.29%**

Physical and Chemical properties	**+/-**	
TiO_2 concentration (%w/w)	0.5	**6**
Density (g/ml)	0.05	1.15
Viscosity 20°C (mPas/sec)	0.1	2
Nanoparticle size (nm)	-	30
Polydispersity index (pdI)	0.05	0.25
pH	0.5	5.5

Supplier: Colorobbia Italia spa

US 2008/0317959 A1, Dec. 25, 2008.
Method for preparation of aqueous dispersion of TiO_2 in the form nanoparticles, and dispersions obtainable with this method.
Inventors: Baldi G. et al.

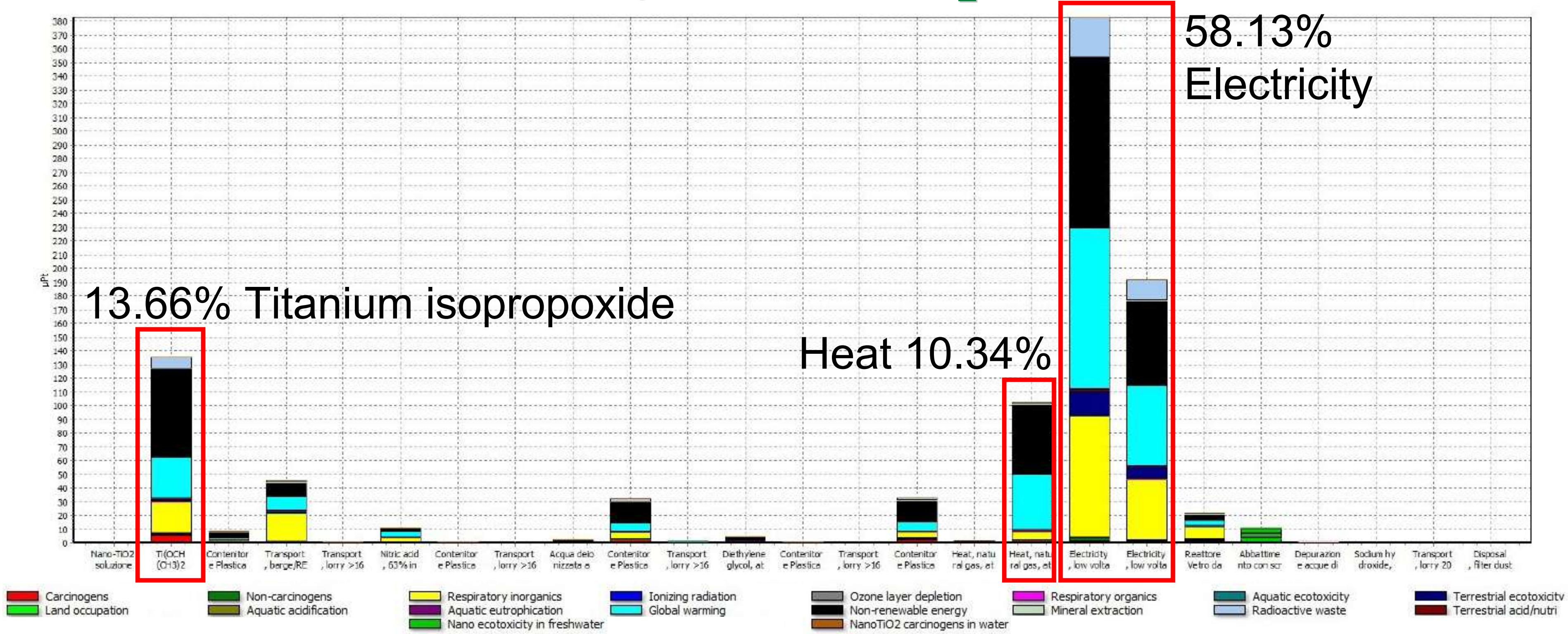
1. LCA of nanoTiO_2 suspension

- Goal definition: assess the environmental impacts of the nanoTiO_2 suspension obtained by a liquid-phase process.
- Functional unit: multi output process

Products	UF	Unit	Mass allocation
Nano TiO_2 suspension	0.75425=1kg*88%*85.71%	kg	75.425%
Coproduct			
Isopropanol	0.12=1kg*12%	kg	12%
H_2O deionized	0.12575=1kg*88%*14.29%	kg	12.575%

- Function of the system: functionalize building materials.
- System boundaries: "*from cradle to gate*".
- Data quality: primary data and secondary data (literature and DB data).
- Calculation software: SimaPro 7.3.3
- Impact method: modified IMPACT 2002+

1. LCIA of 1kg of nanoTiO_2 suspension



Impact category	Amount
Non-renewable energy	36.6%
Global warming	29.2%
Respiratory inorganics	21.3%
Nano ecotoxicity in fresh water	3.4E-6%
NanoTiO2 carcinogens in water	6.75E-7%

Total damage: 0.989 mPt



Life Cycle Assessment of nanoTiO_2 coatings


«from cradle to grave»

SimaPro 7.3.3

Modified IMPACT 2002+


Life Cycle Assessment of nanoTiO_2 coatings

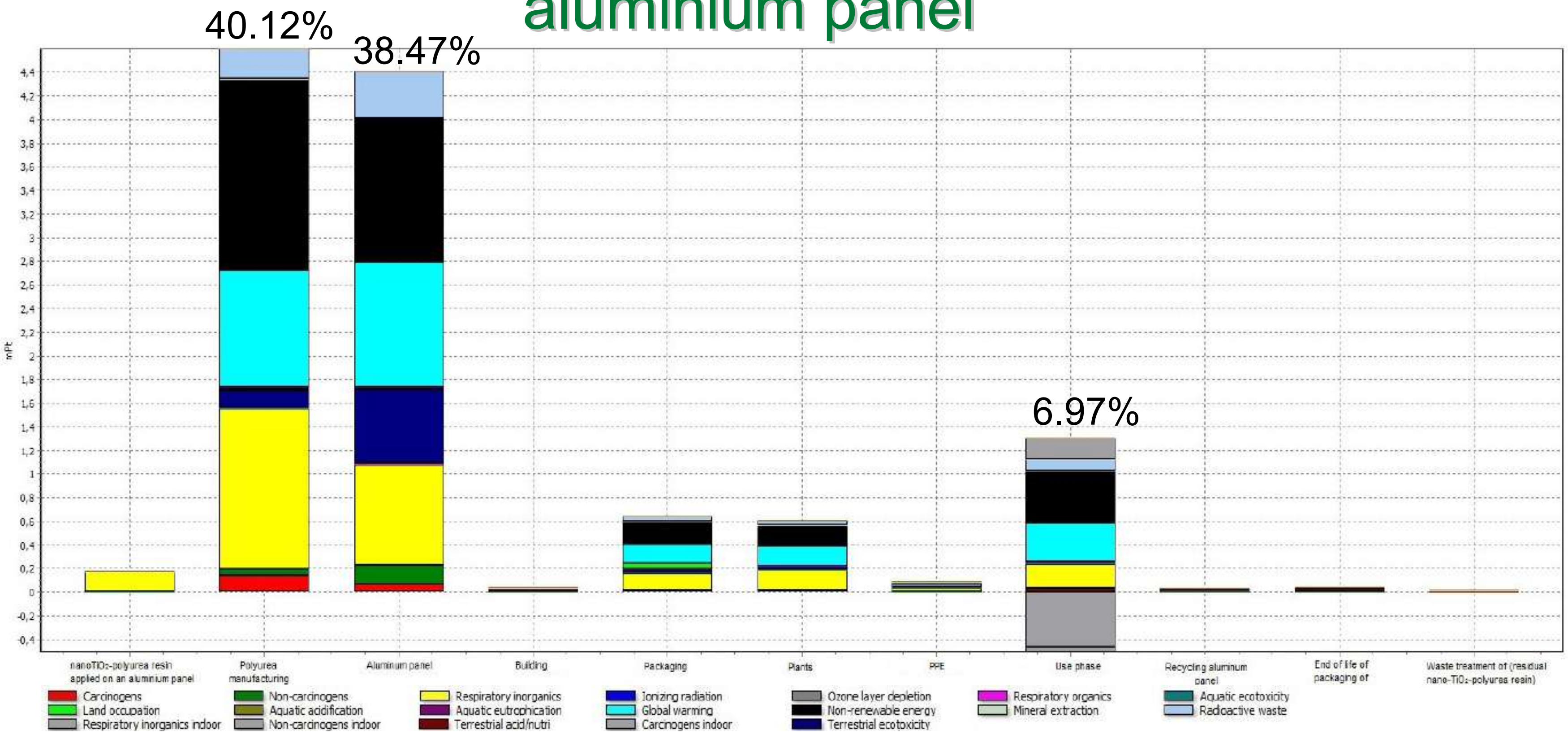
Studied System	System Function	Funtional unit	Life time	Damage	Benefits
nanoTiO_2-polyurea resin applied on an aluminium panel	INDOOR coating surface with self-cleaning and self-sterilized functions	3 m^2	20 years	OUTDOOR and INDOOR Emissions ✓Application step ✓Use phase ✓End of life	INDOOR NO_2 reduction E. Coli reduction ✓Use phase
nanoTiO_2 coating applied on a float glass	OUTDOOR coating surface with self-cleaning and solar factor reduction functions	h * l m^2	20 years	OUTDOOR and INDOOR Emissions ✓Application step ✓Use phase ✓End of life	OUTDOOR NO reduction VOC reduction ✓Use phase
nanoTiO_2-glaze applied on an steel panel	OUTDOOR coating surface with self-cleaning and anti-smog functions	h * l m^2	20 years	OUTDOOR and INDOOR Emissions ✓Application step ✓Use phase ✓End of life	OUTDOOR NO reduction VOC reduction ✓Use phase

Ecodesign approach

- Installation of HEPA (*High Efficiency Particulate Air filter* → 99.97%) air filter where there is the risk to have a release of nanoparticle emissions.
- Closed manufacturing system
- Use of specific packaging to limit the release of nanoparticle emissions during the transports.
- PPE (*Personal Protective Equipment*): face mask with 95% of efficiency.
- Waste treatment:

nanoTiO_2-polyurea applied on an Al panel	Heat treatment, T=660°C: Recycling of aluminum panel (melting point: 660°C) Evaporating of the residual nanoTiO_2-polyurea resin (melting point: 350°C)
nanoTiO_2-coating applied on a float glass	Making inert the float glass with nanoTiO_2 coating
nanoTiO_2-glaze applied on an steel panel	Making inert the steel panel with nanoTiO_2 coating

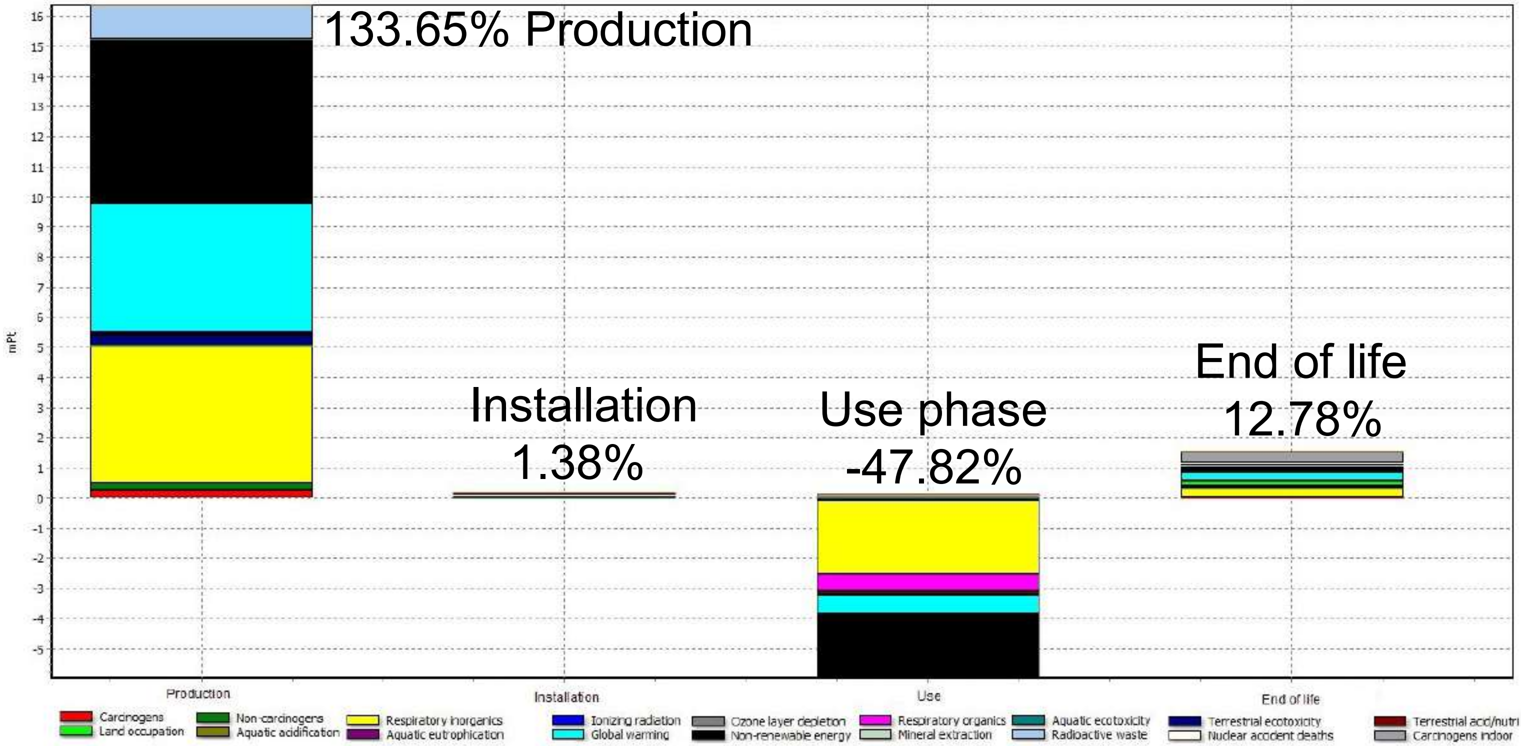
2. LCIA of 1 m^2 of nanoTiO_2-polyurea resin applied on an aluminium panel



Impact category	Amount
Non-renewable energy	32%
Global warming	25.86%
Respiratory inorganics	23.98%
Carcinogens indoor	1.60%
Non-carcinogens indoor	-0.36%
Respiratory inorganics indoor	-4.06%

Total damage: 11.456 mPt

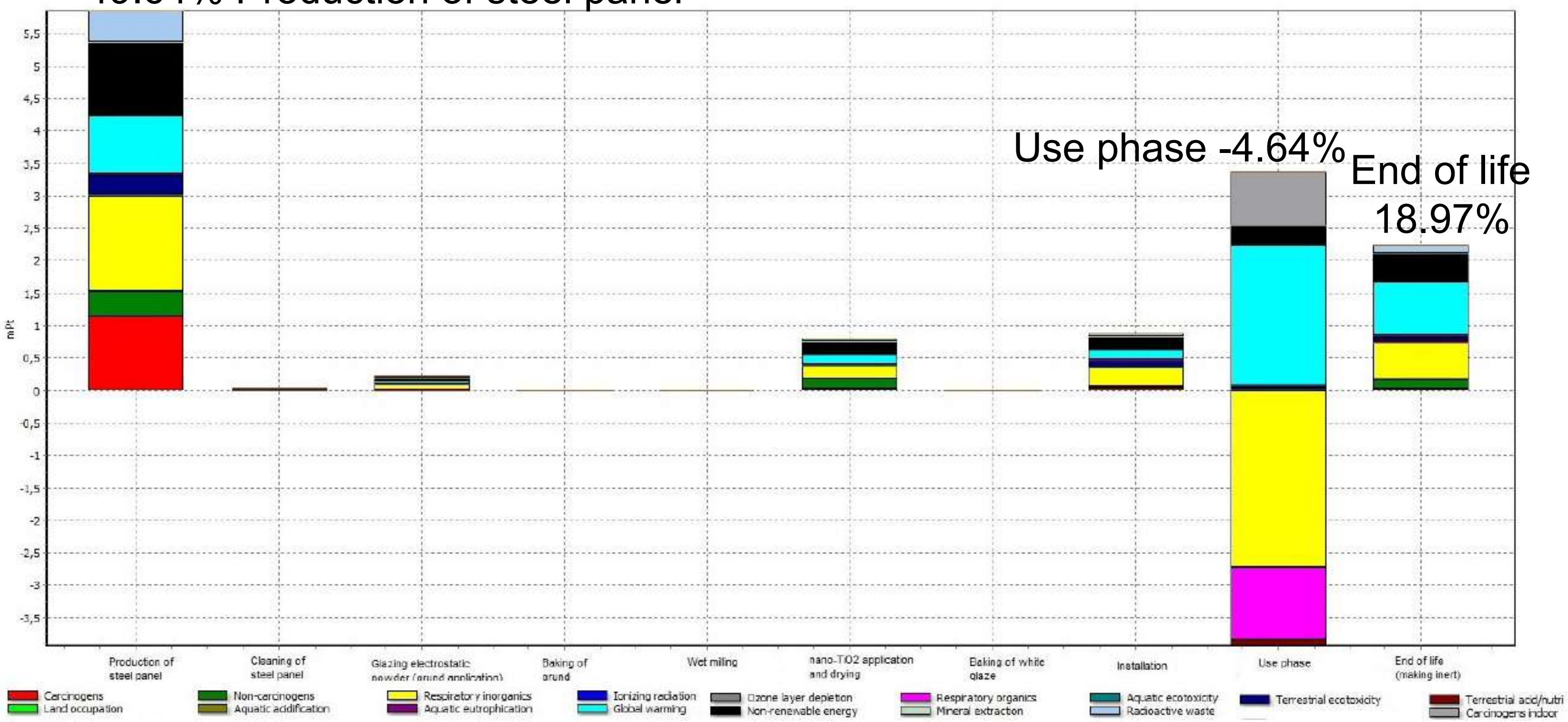
3. LCIA of 1 m^2 nanoTiO_2 coating applied on a float glass



Impact category	Amount
Global warming	31.87%
Non-renewable energy	29.87% (46.7%-16.84%)
Respiratory inorganics	19.84% (39.84%-20%)
Carcinogens indoor	4.76%
Respiratory organics	-4.52%

Total damage: 12.224 mPt

4. LCIA of 1 m^2 of nanoTiO_2-glaze applied on an steel panel



Impact category	Amount
Global warming	39.5%
Non-renewable energy	22.3%
Carcinogens	10.87%
Carcinogens indoor	7.04%
Respiratory inorganics	6.88% (30%-23.12%)
Respiratory organics	-9.47%

Total damage: 11.78 mPt

Conclusions and remarks

- Damage of nanoTiO_2: the Use Phase and End of life are the more affected life cycle steps.
- Parametric analysis → varying % of nanoparticle emissions, TiO_2 concentration and filter efficiency.
- Nanotoxicological indicators: this is a preliminary research to evaluate the risks and the safe use of nanoparticles.
- The LCA case studies follow the Ecodesign approach giving a guidance on how it should be the production, the handling, the transport, the end of life of nanoparticles/nanomaterials.
- Assessment of the actual environmental performance of functionalized building materials once embedded in entire building.

Case study: Municipio di Fiorano Modenese.

Thank you for your attention

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