A proposal for the derivatization of characterization factors for CdTe Quantum dots that integrates changing particle sizes throughout their life cycle

María Blázquez[1,2*], Tom Ligthart[3], Beatriz Corral[4], Bas Henzing[3], Harrie Buist[5], Ralph Rosenbaum[6], Miren P. Cajaraville[2]

1 INKOA SISTEMAS, Ribera de Axpe 11, Edificio D1 Dpto 208. 48950 Erandio, Spain

2 CBET Research Group, Department of Zoology and Animal Cell Biology; Faculty of Science and Technology and Research Centre for Experimental Marine Biology and Biotechnology PiE, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain

3 Netherlands Organisation for Applied Scientific Research TNO, Location Utrecht, PO Box 80015, 3508 TA Utrecht, the Netherlands

4 EKOTEK, Ribera de Axpe 11, Edificio D1 Dpto 208. 48950 Erandio, Bizkaia, Spain

5 Netherlands Organisation for Applied Scientific Research TNO, Location Zeist, PO Box 360, 3700 AJ Zeist, the Netherlands

6 Institute for Research and Technology in Agrifood, IRTA, Torre Marimon, 08140 Caldes de Montbui, Spain

**corresponding author (maria@inkoa.com)*

INTRODUCTION & OBJECTIVE

- Even if it has been claimed that Life Cycle Assessment (LCA) is an essential tool to analyze, evaluate, understand and manage the environmental and health impacts of nanotechnology, few studies incorporate **characterization factors (CFs)** for **human toxicity** and **freshwater ecotoxicity** accounting for the impacts of engineered nanomaterials (ENMs) beyond their manufacturing stage.
- The USEtox® model, which is the UNEP-SETAC consensus methodology for freshwater ecotoxicity and human toxicity CFs calculation to be used in Life Cycle Impact Assessment (LCIA), estimates CFs by multiplying three other aggregated parameters related to fate (fate factor, FF), exposure (exposure factor, XF), and toxicity (effect factor EF), respectively, of a specific chemical. The aim of the present work was to compare and combine the **USEtox® model** (which is not nanospecific) and the **SimpleBox4Nano (SB4N) model** (which accounts for nanospecific processes, e.g. aggregation, attachment and dissolution for FF derivatization) taking into consideration their specific features.
- The suitability of the proposed approach has been assessed in an ENM case study consisting of **polyethyleneglycol-coated cadmium telluride (PEG-CdTe) quantum dots (QDs)**. To such purpose, existing information on the (eco)toxicological impact of this ENM has been evaluated and selected to be used for Human Health and Freshwater Ecotoxicity EF derivatization. Additionally, sizes representative of pristine PEG-CdTe QDs and emissions during inkjet printing of a water based ink incorporating them have been experimentally derived under controlled conditions.

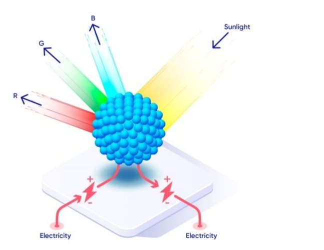
MATERIALS & METHODS

Human Health & Freshwater toxicity data compilation

Freshwater Environmental Effect	**avlogEC_{50}**	log(mg.L^{-1})
Human Health Effect	**ED_{50}inh,noncanc**	kg.lifetime^{-1}
	ED_{50}ing,noncanc	
	ED_{50}inh,canc	
	ED_{50}ing,canc	

Size approximation to other ENMs

Definition of size ranges



Pristine CdTe QDs

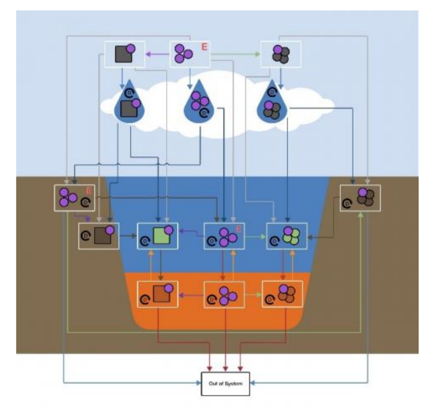
SMPS
Emissions during use phase [60' Printing]

Model's integration – Size-dependent FF (SB4N) – CF (USEtox)

USEtox®

Scientific Consensus Model
Chemical Toxicity Assessment

SimpleBox4Nano



RESULTS

Table 1: Human Health EF (HEF) for LCA, chronic inhalation exposure, for various nanoparticles derived by (Buist et al., 2017). Disability-adjusted life-years (DALYs) have been calculated based on a specific surface area (SSA) of 286 m^2/g for CdTe QDs. Cases have been calculated based on 0.23 DALYs/case for chronic obstructive pulmonary disease (COPD) (see Buist et al. (2017)).

Nanoparticle	Values (DALYs $(m^2/g)^{-1}$ kgintake^{-1}	Equivalent HEF PEG-CdTe QDs	
		DALYs · kgintake^{-1}*	Cases · kgintake^{-1}#
Carbon black	0.0067	1.9	8.3
MWCNT – Baytubes	125	125	540
Ag	0.15	42.9	186.5
TiO2	0.013	3.7	16.2

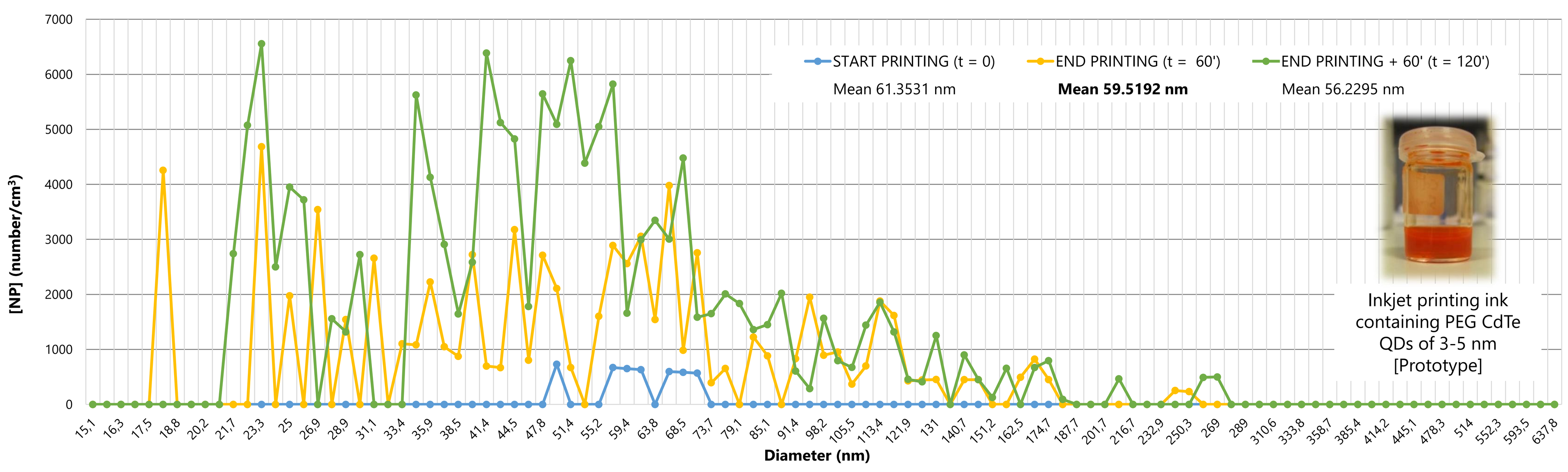
The chronic HEF of the PEGylated CdTe could be between 1.9 and **125** DALYs kg_{intake}^{-1} for **LOW HUMAN TOXICITY** and **HIGH HUMAN TOXICITY**, respectively. Non-carcinogenic effects are considered only.

Table 2: Freshwater toxicity data selected for Environmental EF Calculation

Species	Trophic Level	Reference	Endpoint	Time (h)	EC_{50} (mg/L)	Chronic
Chlamydomonas reinhartii	Algae	Wang et al (2008)	Growth	72 (Acute)	5.000	2.50
Daphnia pulex	Crustacean	Tang et al (2015)	Death	48 (Acute)	0.250	0.125
Danio rerio	Fish	Zhang et al (2012)	Death	120 (Acute)	15.280	7.64

Taking into consideration data reported in Table 2 an (interim) ecoEF corresponding to 374.10 Potentially Affected Fraction (PAF) m^3/kg is proposed.

Figure 1: Particle size of emissions measured at the start of the printing process (t=0); at the end of the printing process (t=60'), and 60' starting from the end of the printing process (t=120'). Mean particle size at the end of the printing process corresponds to 59.5192 nm. SMPS Model 3936L25, TSI Inc.



Mean particle size of pristine CdTe QDs: 3.6 nm

Mean particle size of emissions during 60' inkjet printing: 59.5 nm

Table 3: CdTe QDs CF Calculation based on the adapted value for USEtox® – SB4N for HIGH-human toxicity and freshwater toxicity data (AIR Compartment data shown)

Exposure Compartment	Air	
Considered size (diameter, nm)	**3.6 (Pristine)**	**59.5 (Usage)**
Midpoint Human Toxicity Potential [CTUh = cases.$kg_{emitted}^{-1}$]		
Non-cancer	1.27E-02	1.27E-02
Endpoint Human Toxicity Potential [CDUh = DALY.$kg_{emitted}^{-1}$]		
Non-cancer	2.93E-03	2.93E-03
Midpoint Ecotoxicity Potentials [CTUe $Kg_{emitted}^{-1}$ = PAF.m^3.day.$kg_{emitted}^{-1}$]		
Freshwater ecosystems	2.09E-03	2.35E-03
Endpoint Ecotoxicity Potentials [CDUe $Kg_{emitted}^{-1}$ = PDF.m^3.day.$kg_{emitted}^{-1}$]		
Freshwater ecosystems	1.05E-03	1.17E-03

Figure 2: Integration of USEtox® and SB4N

1. Introduction of basic data for pristine CdTe in SB4N
2. Definition of the USEtox_Air, USEtox_Soil and USEtox_Water scenarios in SB4N
3. Integration of USEtox® values in SB4N for parameters shared by both models
4. Selection of rate constants that are common for both models
5. Introduction of basic substance data for pristine CdTe in USEtox®
6. Introduction of human health values and ecotoxicity values in USEtox®
7. Introduction in USEtox® of the fate values calculated by the adapted SB4N

CONCLUSIONS

- The possibility to combine and integrate the two selected models (USEtox®, SB4N) appeared to be limited since there was no absolute correspondence between parameters and compartments defined by each model. Despite this fact, an approach has been proposed and **CFs are available per two different size classes,** representative of the manufacturing and usage stages, that integrate the formerly developed EF both for freshwater ecotoxicity and human health impact (high toxicity potential and air compartment data shown only).
- The approach hereby proposed, despite limitations referred, allows taking into account **specific data on ENMs for LCIA beyond the manufacturing stage**. Its relevance relies on the fact that CFs can be calculated accounting for the mean size of emitted particles throughout the life cycle of CdTe QDs incorporating products in combination with (eco)toxicological information.

References:

Buist et al., (2017). Derivation of health effect factors for nanoparticles to be used in LCIA. *NanoImpact*, 7. https://doi.org/10.1016/j.impact.2017.05.002

Meesters et al., (2014) Multimedia Modelling of Engineered Nanoparticles with SimpleBox4nano: Model Definition and Evaluation. *Environmental Science and Technology* 48, 5726−5736. Official page of the SimpeBox4Nano model (https://www.rivm.nl/en/soil-and-water/simplebox4nano)

Rosenbaum et al., 2008. USEtox - The UNEP-SETAC toxicity model: Recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *International Journal of Life Cycle Assessment* 13, 532-546. Official page of the USEtox model: (www.usetox.org)

Tang et al., (2015). Distinct expression profiles of stress defense and DNA repair genes in Daphnia pulex exposed to cadmium, zinc, and quantum dots. Chemosphere, 120. https://doi.org/10.1016/j.chemosphere.2014.06.011

Wang et al., (2008). Toxicity assessment of manufactured nanomaterials using the unicellular green algae *Chlamydomonas reinhardtii*. *Chemosphere*, *73*(7). https://doi.org/10.1016/j.chemosphere.2008.07.040

Zhang et al., (2012). Toxicity assessment of zebrafish following exposure to CdTe QDs. *Journal of Hazardous Materials*, 213–214. https://doi.org/10.1016/j.jhazmat.2012.02.014

LCM 2021

Acknowledgments

This work was supported by:

The European Union's Seventh Framework Programme (EU FP7) GA No. 309329 (NanoSolutions)

The European Community Research Infrastructures; FP7 Capacities Programme GA No. INFRA-2010-262163 (QualityNano)

Basque Government - Grant to the consolidated research group IT810-13 and IT1302-19.

Authors thank PlasmaChem GmbH, specially Alexei Antipov, for providing the PEG-CdTe QDs ink.