Materials Science & Technology

Ecological Exposure
Review of State of Science

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St. Gallen, Switzerland

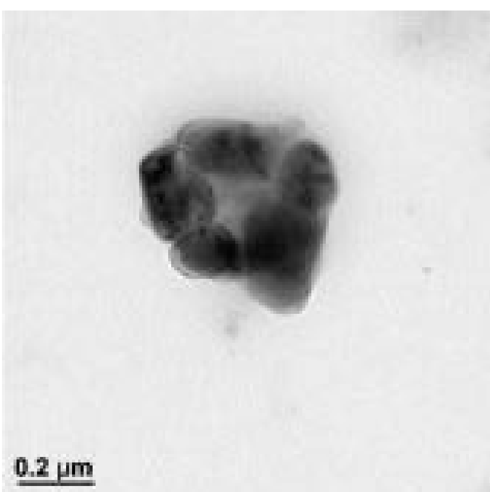
Outline

- Life cycle approach
- Production and use
- Release
- Material Flow Modeling
- Ecological Exposure
- Environmental Risk Assessment

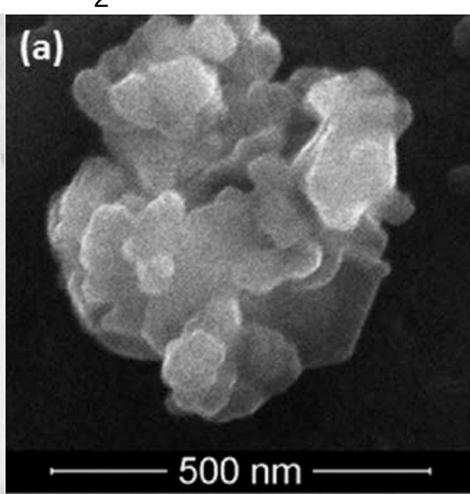
Why not just measure exposure?

- Quantitative trace analysis of <u>engineered</u> nanomaterials in the environment is NOT yet possible
- Nanosized fraction ≠ engineered NM
- Qualitative detection possible

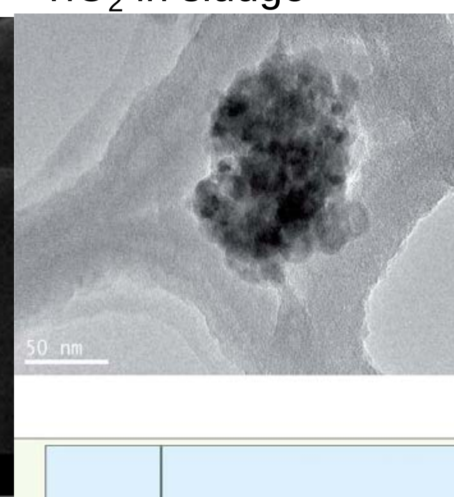
Kaegi (2008)
TiO_2 in stream



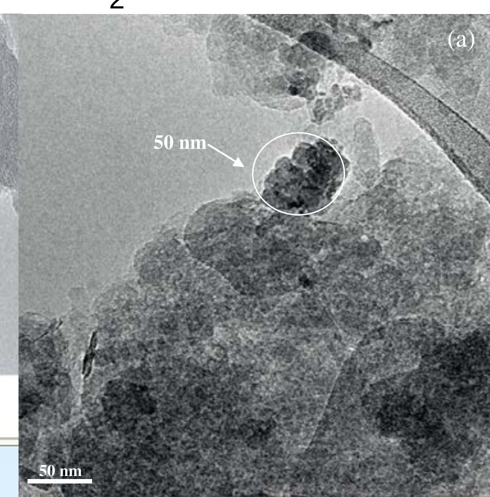
Gondikas (2014)
TiO_2 in lake sediment



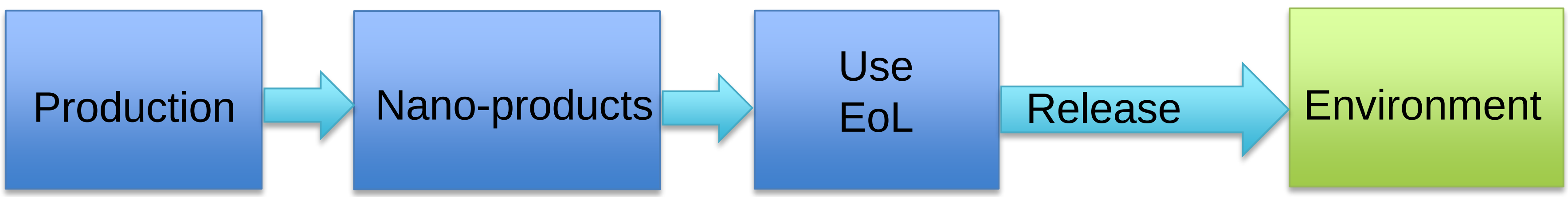
Westerhoff (2011)
TiO_2 in sludge



Yang (2014)
TiO_2 in soil



The life cycle perspective on environmental exposure



Information requirements

- Total amount
- Geographic distribution

- Relative share of product categories

- Life cycle as determinant
- Product type determines release potential

- Amount released
- Transformations
- Form released
- Real-world release

- Fate processes
- Geographic distribution
- Natural NM

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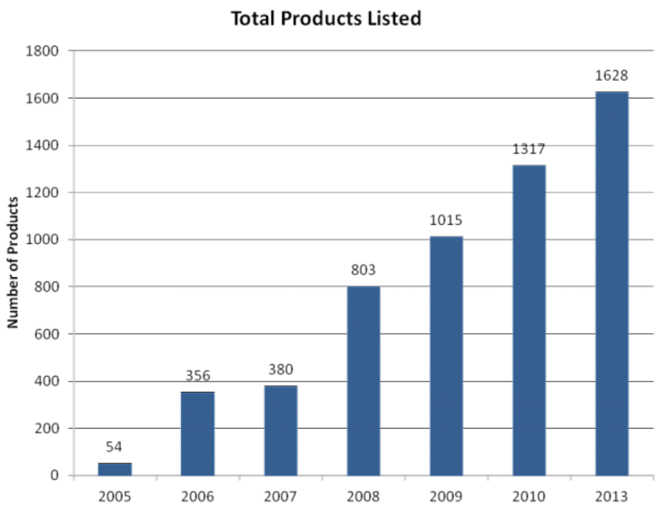
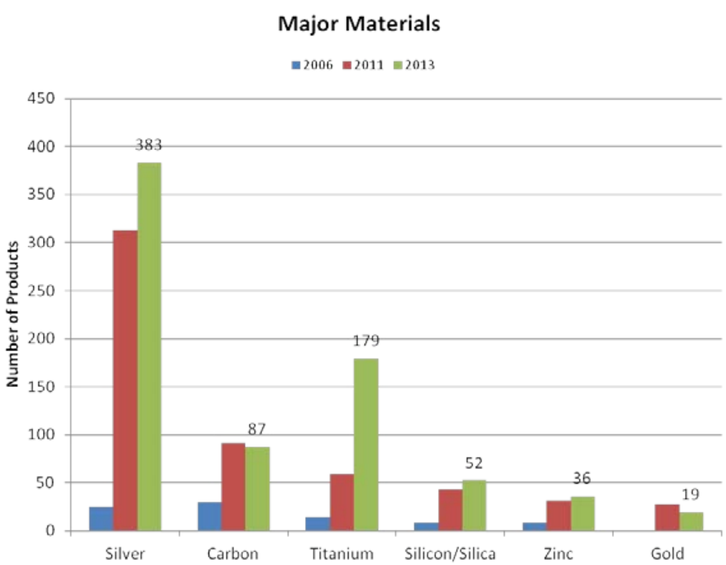
Production/ consumption, extrapolated to the EU (in tons/y)

ENM	(Schmid and Riediker, 2008)	(Hendren et al., 2011)	(Piccinno et al., 2012)	(Keller et al., 2013)	(ANSES, 2013)	Sun et al., 2014
TiO_2	11’500	8’600-42’000	550	20’000	92’000	10,000
Ag	82	3-20	6	100	0.006	30
ZnO	1,900	-	55	7,900	1,900	1,600
CNT	26	60-1,200	550	740	-	380
C_{60}	-	2-90	0.6	-	< 100	20
CeO_2	-	40-770	55	2,300	700	-
Al-ox	0.1	-	550	8,100	15,000	-
Fe-ox	9,700	-	550	9,700	6,100	-
SiO_2	2,000	-	5500	22,000	990,000	-
Nanoclays	-	-	-	2,400	<100	-
Cu	-	-	-	46	< 100	-
Quantum dots	-	-	0.6	-	-	-

Product databases

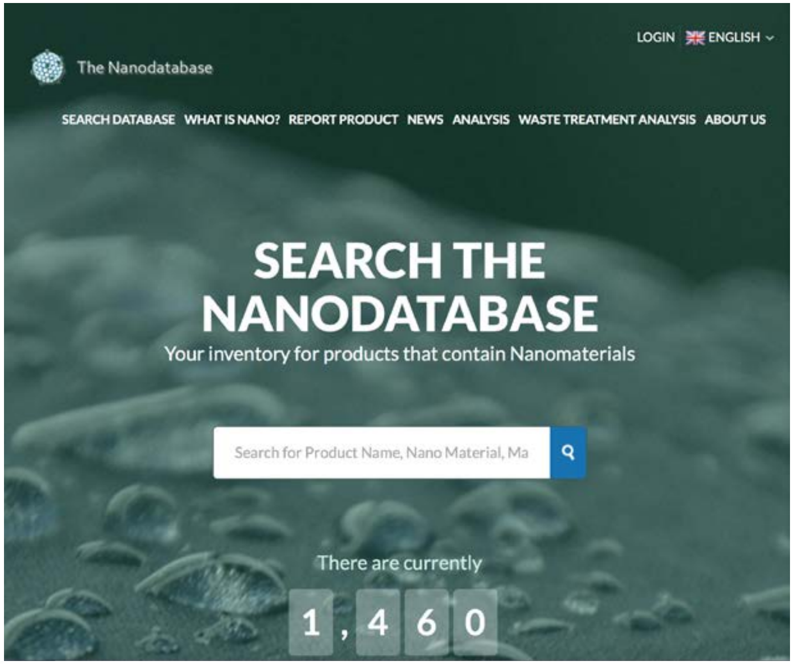
Woodrow Wilson Database

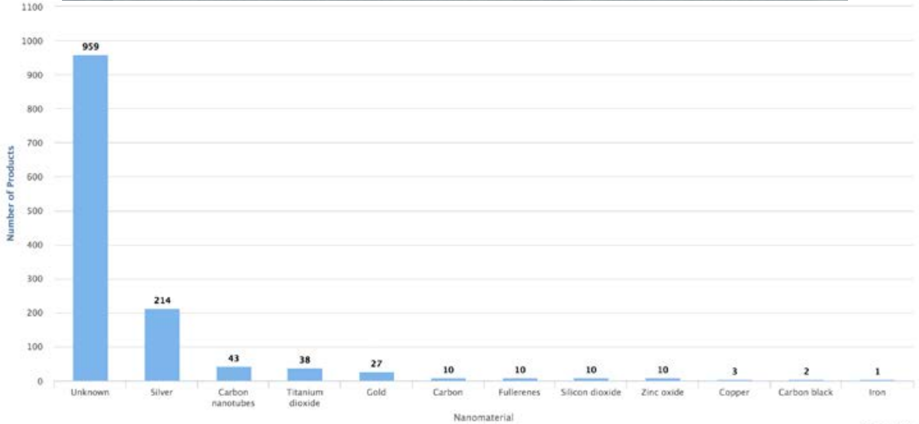




http://www.nanotechproject.org/inventories/consumer/

Danish Nano-Database





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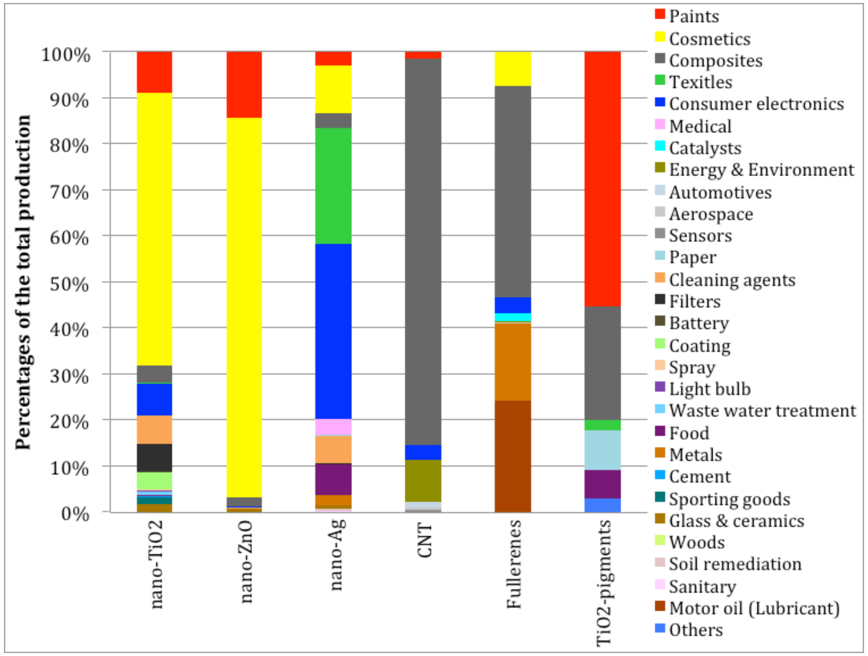
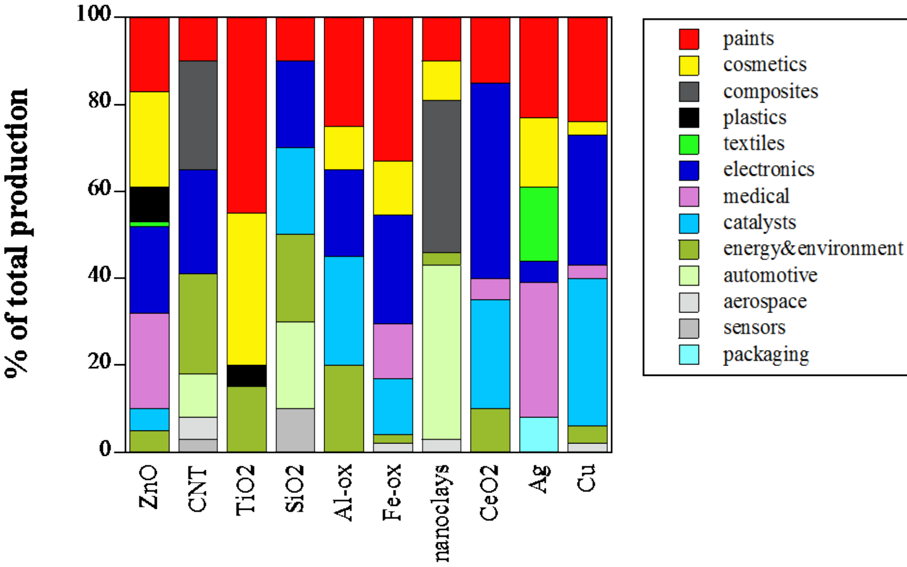
Survey of industry: Uses of nanomaterials

Nanomaterial	Product Group	% of total use
Nano-TiO_2	*Cosmetics (incl. sunscreens)*	*70 – 80*
	Coatings & cleaning agents	*< 20*
	Plastics	*< 20*
	Paints	*10 – 30*
	Cement	*1*
	Others	*< 10*
Nano-ZnO	*Cosmetics (incl. sunscreens)*	*70*
	Paints	*30*
CNTs	*Composites & polymer additives*	*20*
	Materials	*80*
	Composites	50
	Batteries	50
Fullerenes	*R&D*	*80*
Nano-Ag	*Paints, coatings & cleaning agents*	*10 – 30*
	Textiles	*30 – 50*
	Consumer electronics & conductivity	*10 – 20*
	Cosmetics	*20*
	Medtech	*20*
	Anti-microbial coatings	*80 – 100*

Piccinno et al., (2012) *J. Nanopart Res.*, 14: 1109.

Product distribution for nano-product categories





Sun et al., (2014) Environ. Pollut. 185: 69-76

Keller et al., (2013) J. Nanopart. Res. 15:1-17

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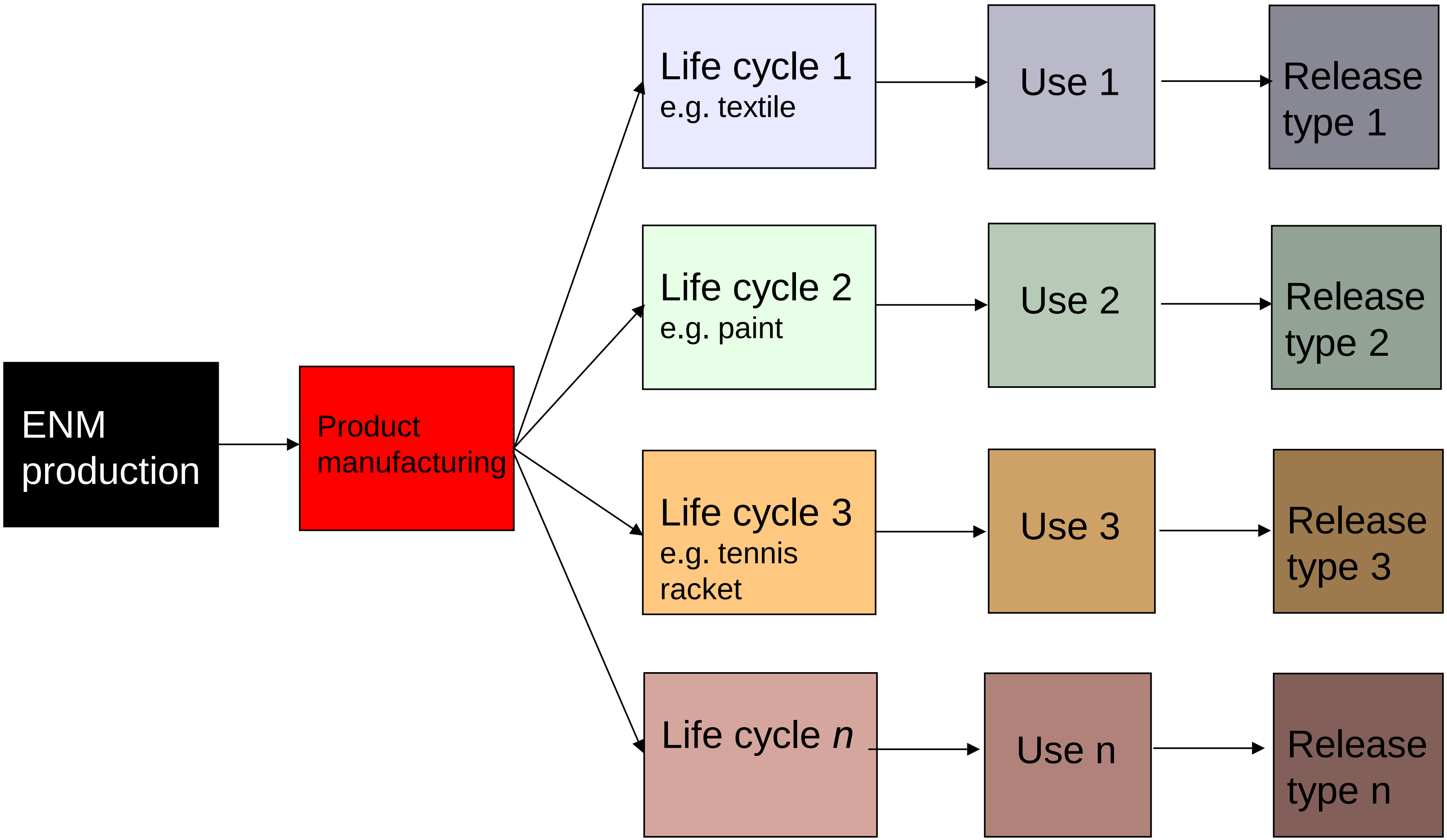
Why care about the life cycle?



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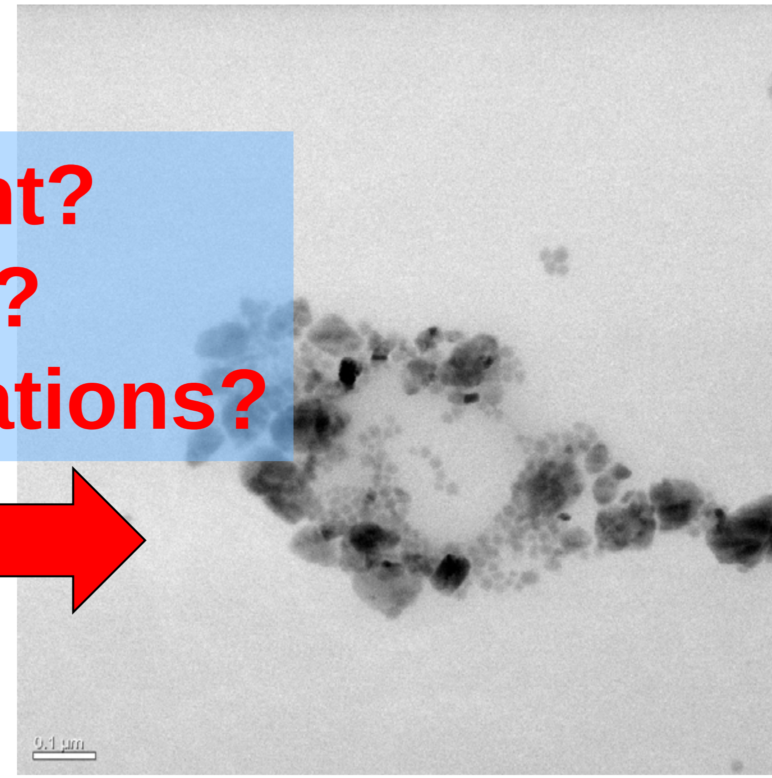
Release determines exposure



Amount?
Form?
Transformations?

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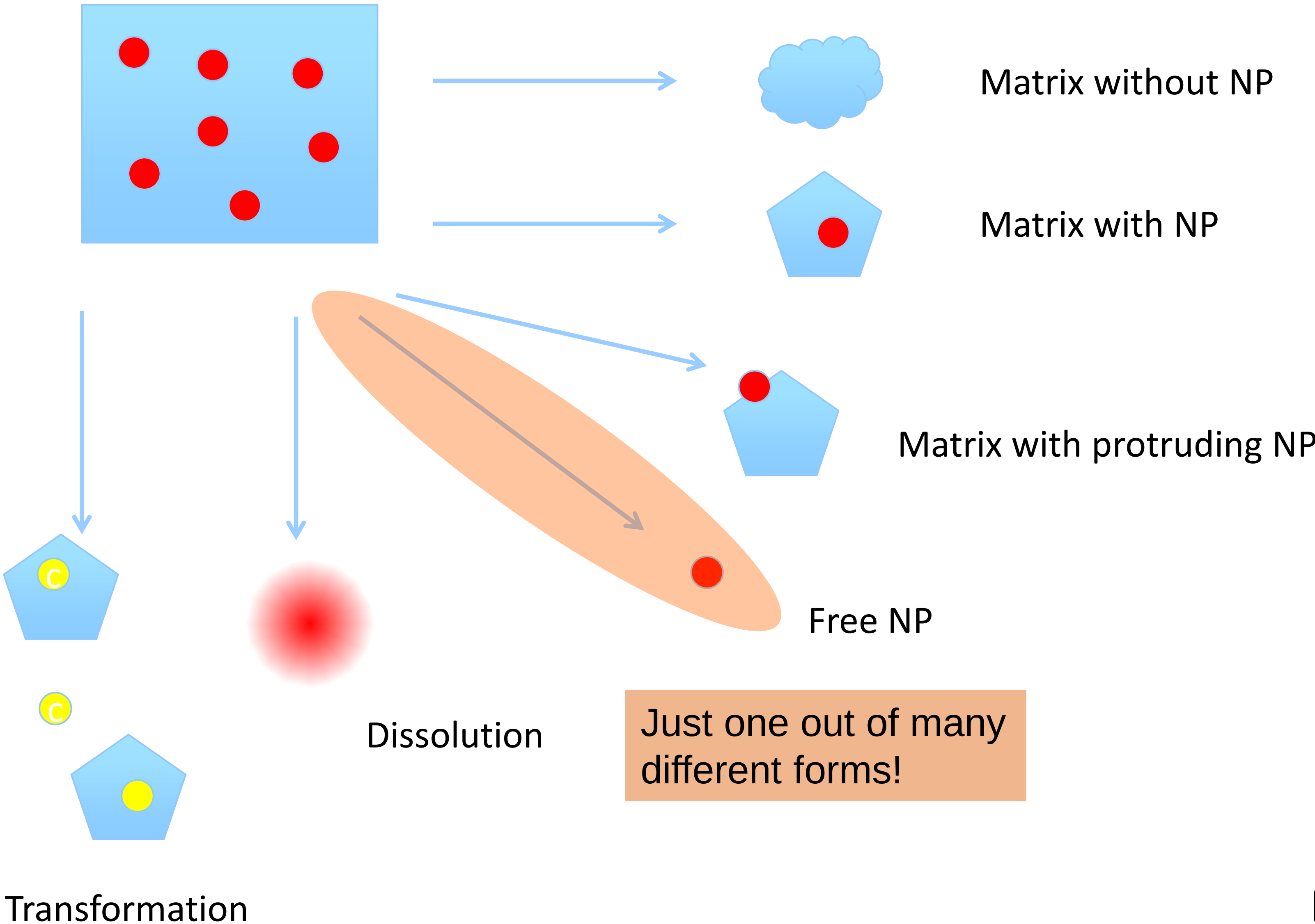
Release during accidents

http://www.lalsace.fr/actualite/2011/10/10/vieux-thann-des-sacs-d-oxyde-de-titane-tombent-d-un-camion-sur-la-rn66#jimage=1446B4B6-C4F4-42B8-8F20-052BEA52339E

Release during accidents

http://www.lalsace.fr/actualite/2011/10/10/vieux-thann-des-sacs-d-oxyde-de-titane-tombent-d-un-camion-sur-la-rn66#jimage=1446B4B6-C4F4-42B8-8F20-052BEA52339E

Characterization of released materials



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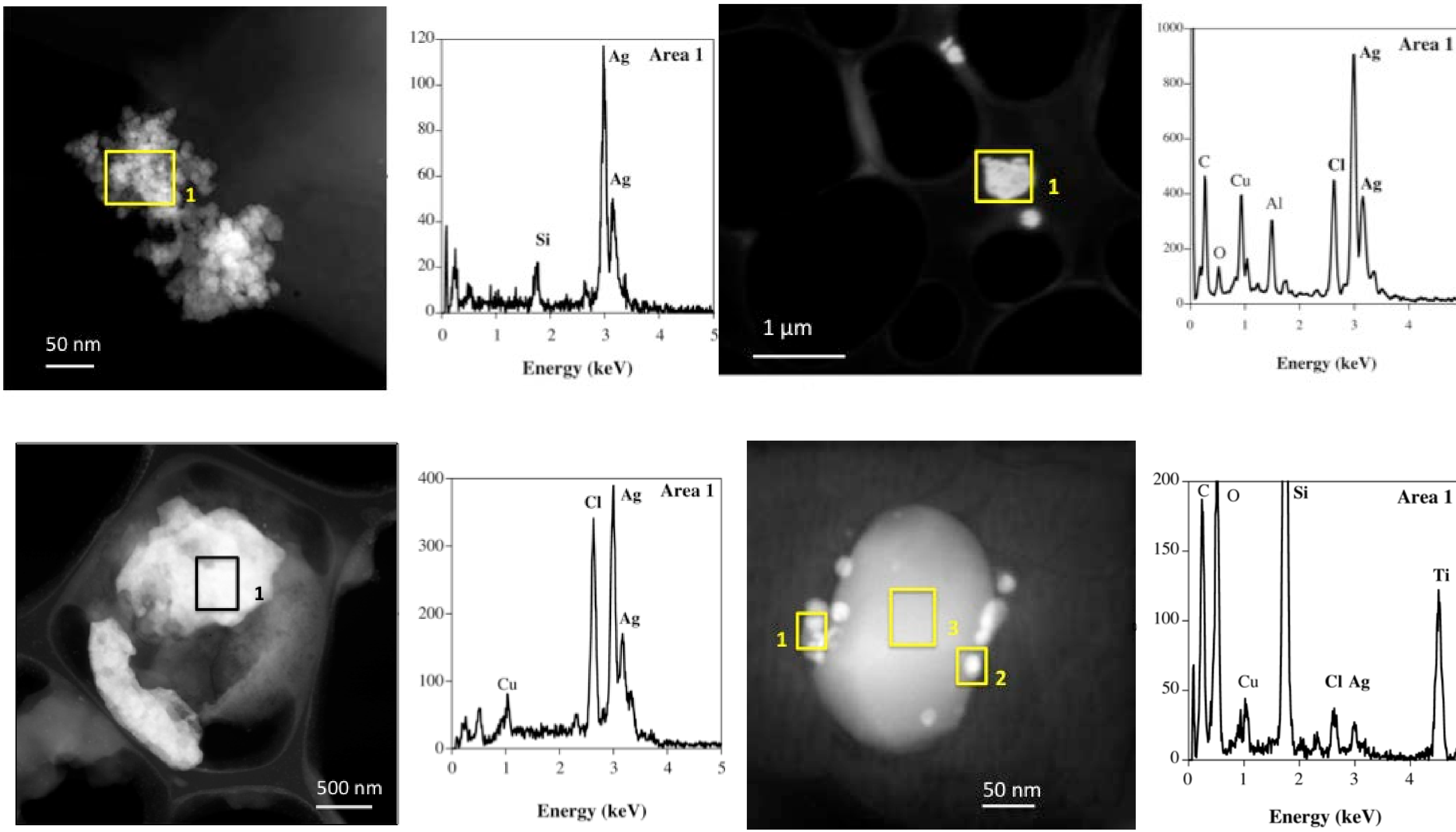
Characterization of released Ag



Lorenz et al., *Chemosphere*, 89: 817–824 (2012)

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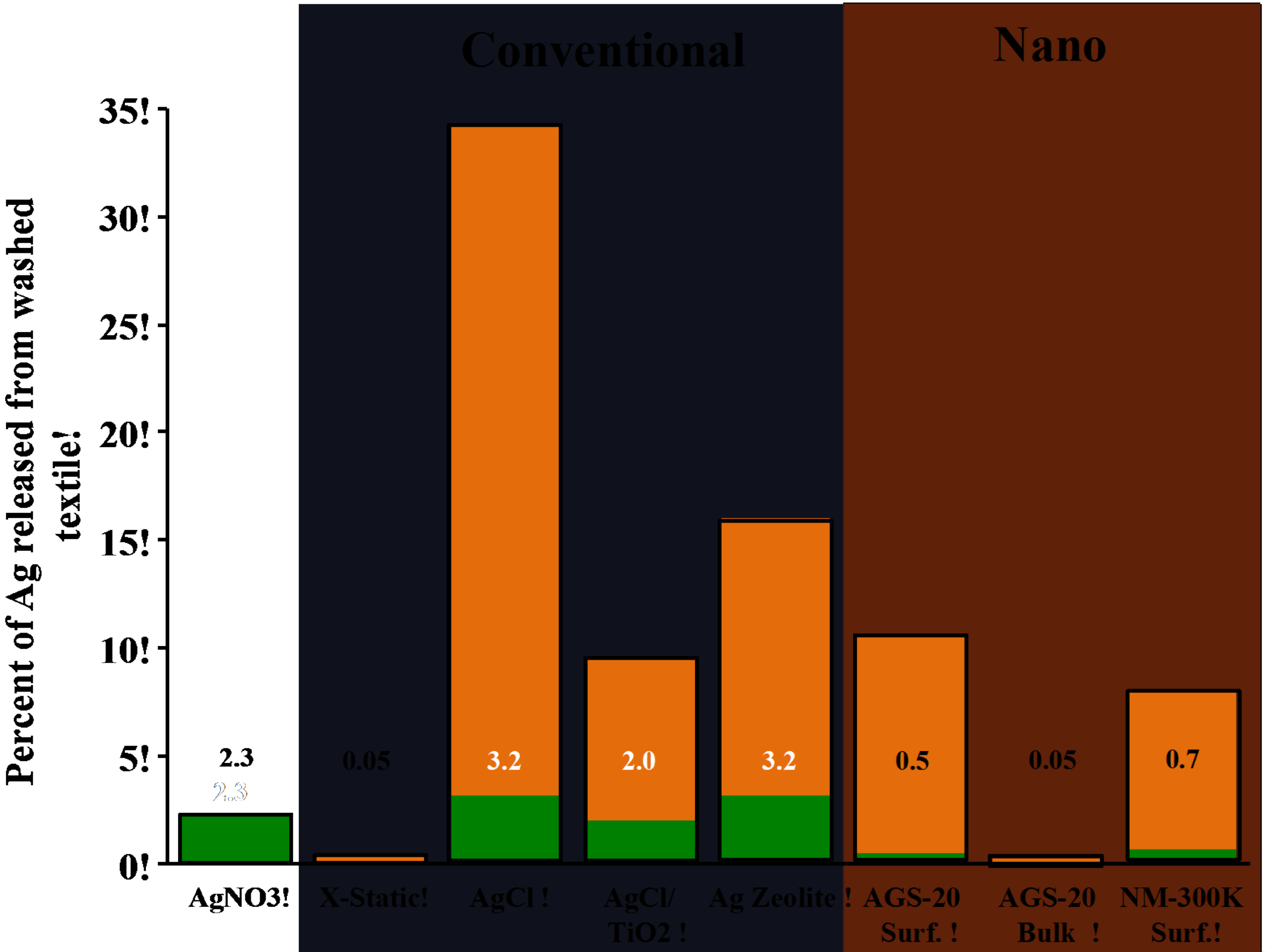
Ag speciation of original and washed textile

	Textile	Ag-NPs	AgCl-NPs	Ag_2S-NPs	Ag oxide	Ag phos.	Ag nitr.	Ag sulf.	Ag-zeolite	R factor
	Unwashed									
Ag integrated in fiber	T1			16 (1.6)			52 (0.7)	14 (0.7)	18 (1.3)	0.0005
Nano-Ag	T4	55 (1.7)	11 (3)	32 (5)						0.0001
Ag ions	T5	43 (1.5)	17 (3)	35 (3)	5 (0.8)					0.0001
Nano-Ag	T6	12 (3)		16 (5)		67 (6)			5 (0.5)	
AgCl	T7	36 (1.7)	36 (3)	14 (2)				14 (1.7)		0.0005

Lombi et al., (2014) Chemosphere 111, 352

Nanomaterial Release from Textiles



Mitrano et al., (2014) ACS Nano 8: 7208

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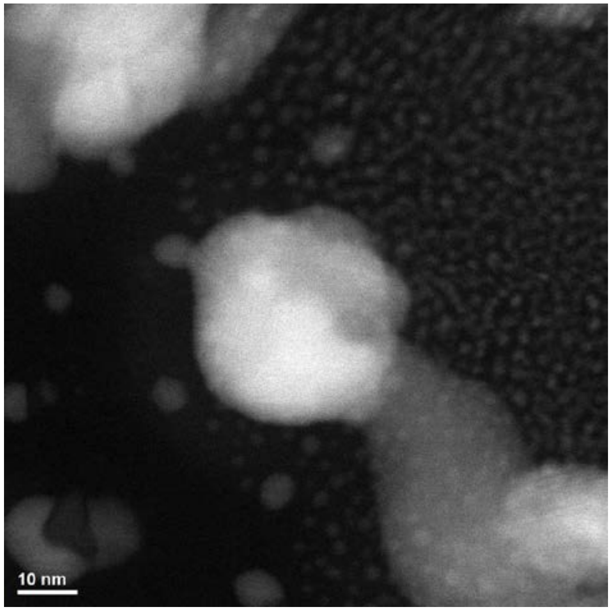
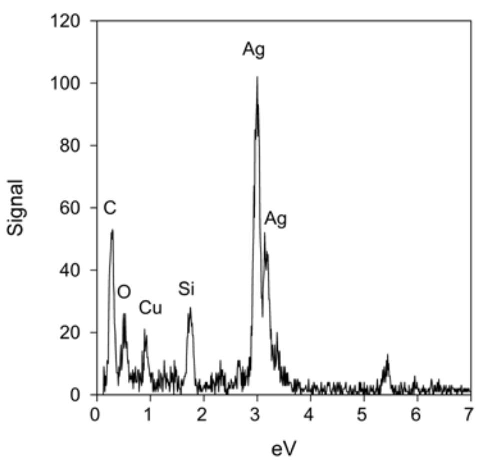
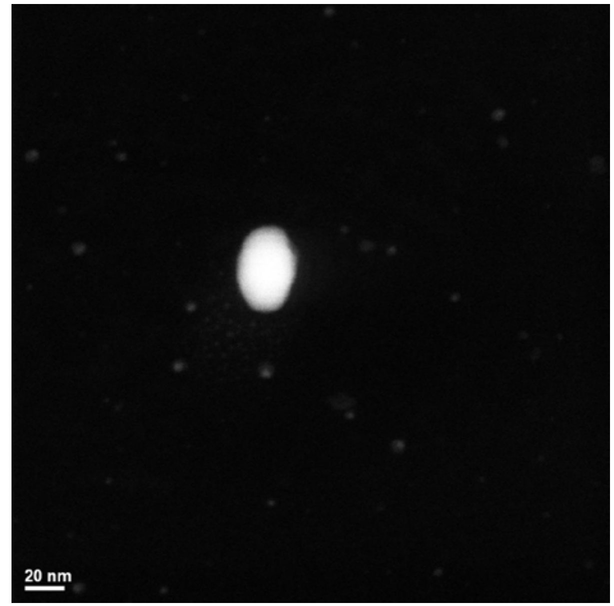
Formation of nano-Ag

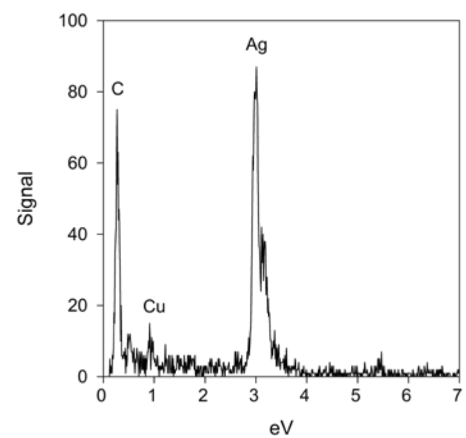
Dissolved Ag





Ag zeolites





Mitrano et al., (2014) ACS Nano 8: 7208

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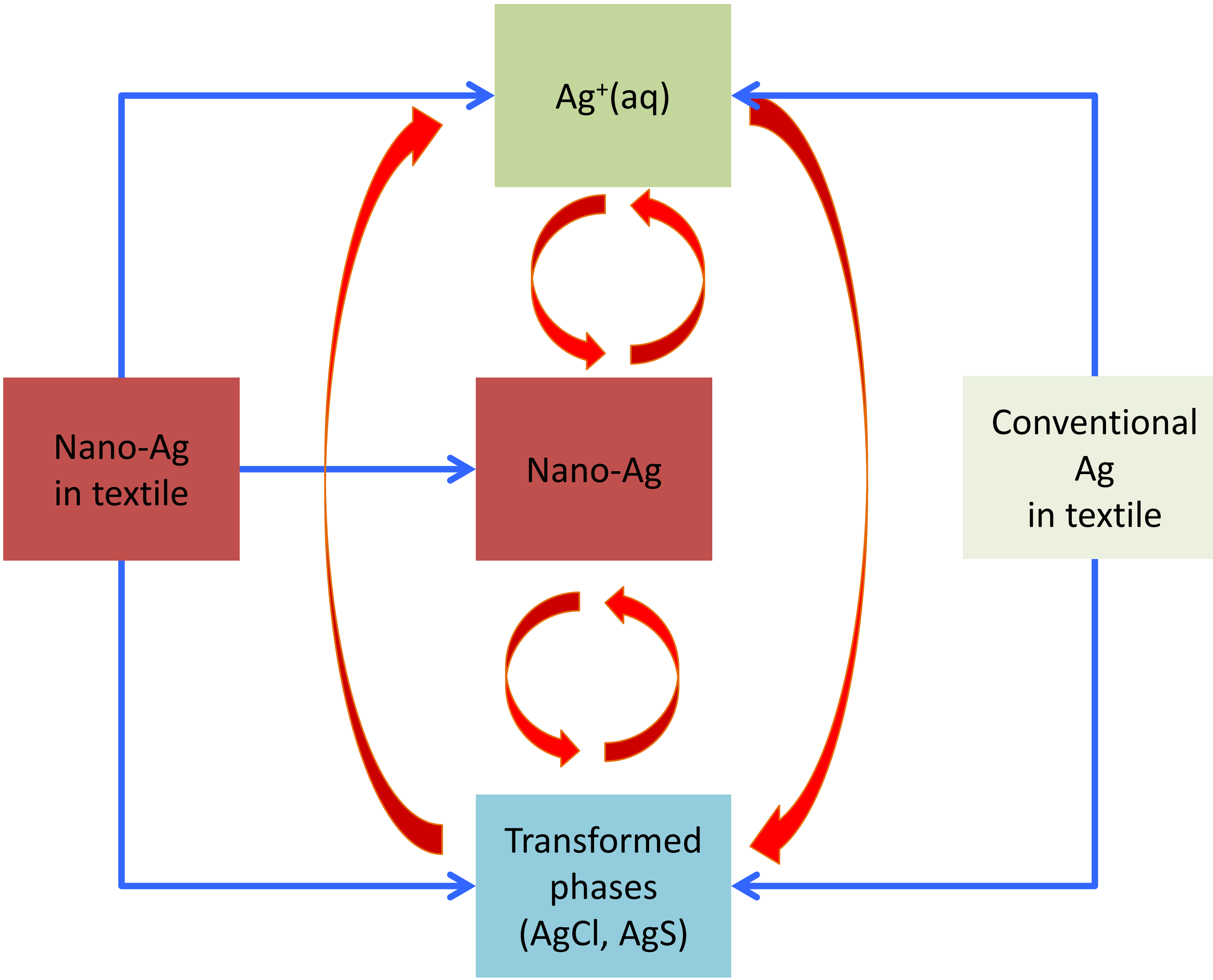
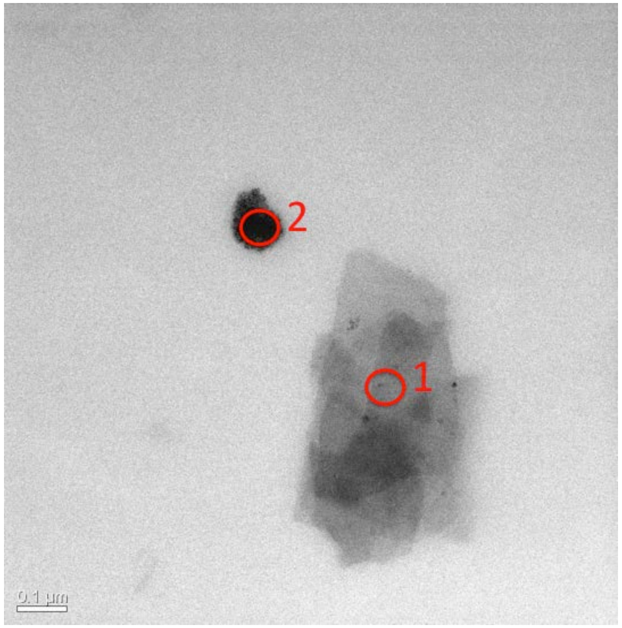
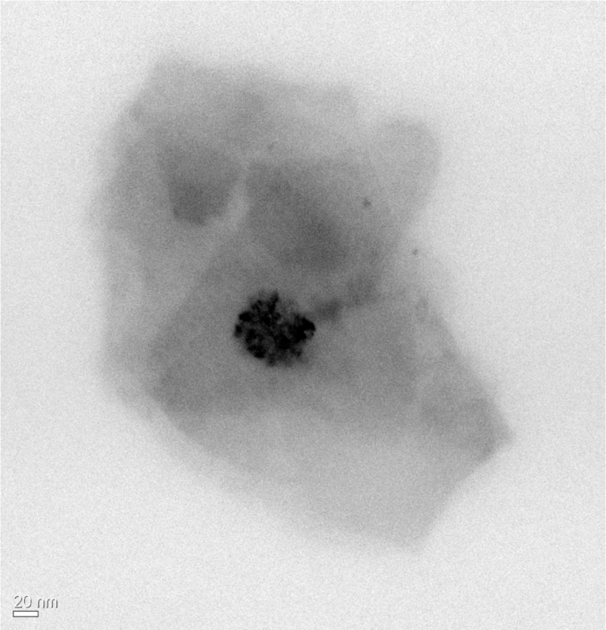
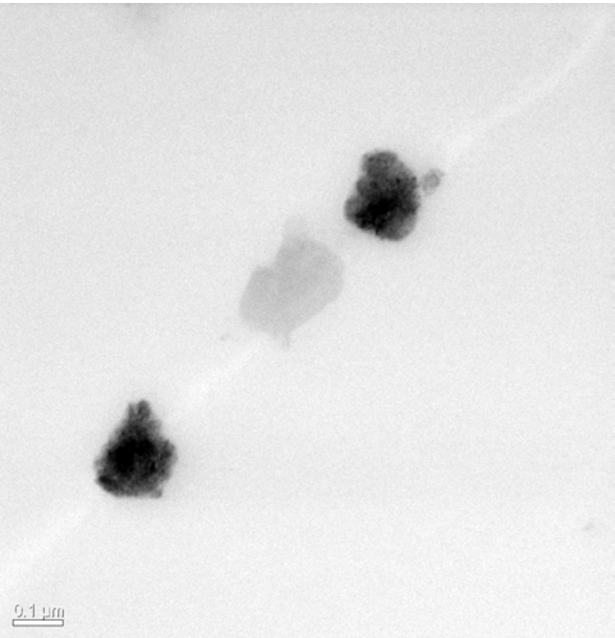
Transformations of Ag released from textiles

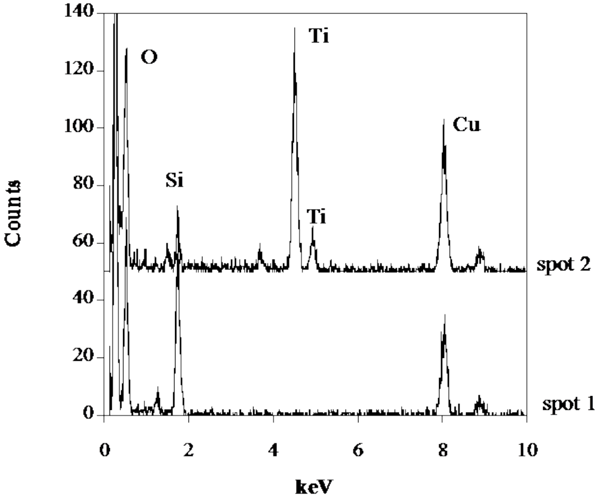


Characterization of released TiO_2









Al-Kattan et al., (2014) *Environ. Sci. Technol.*, 48: 6710−6718

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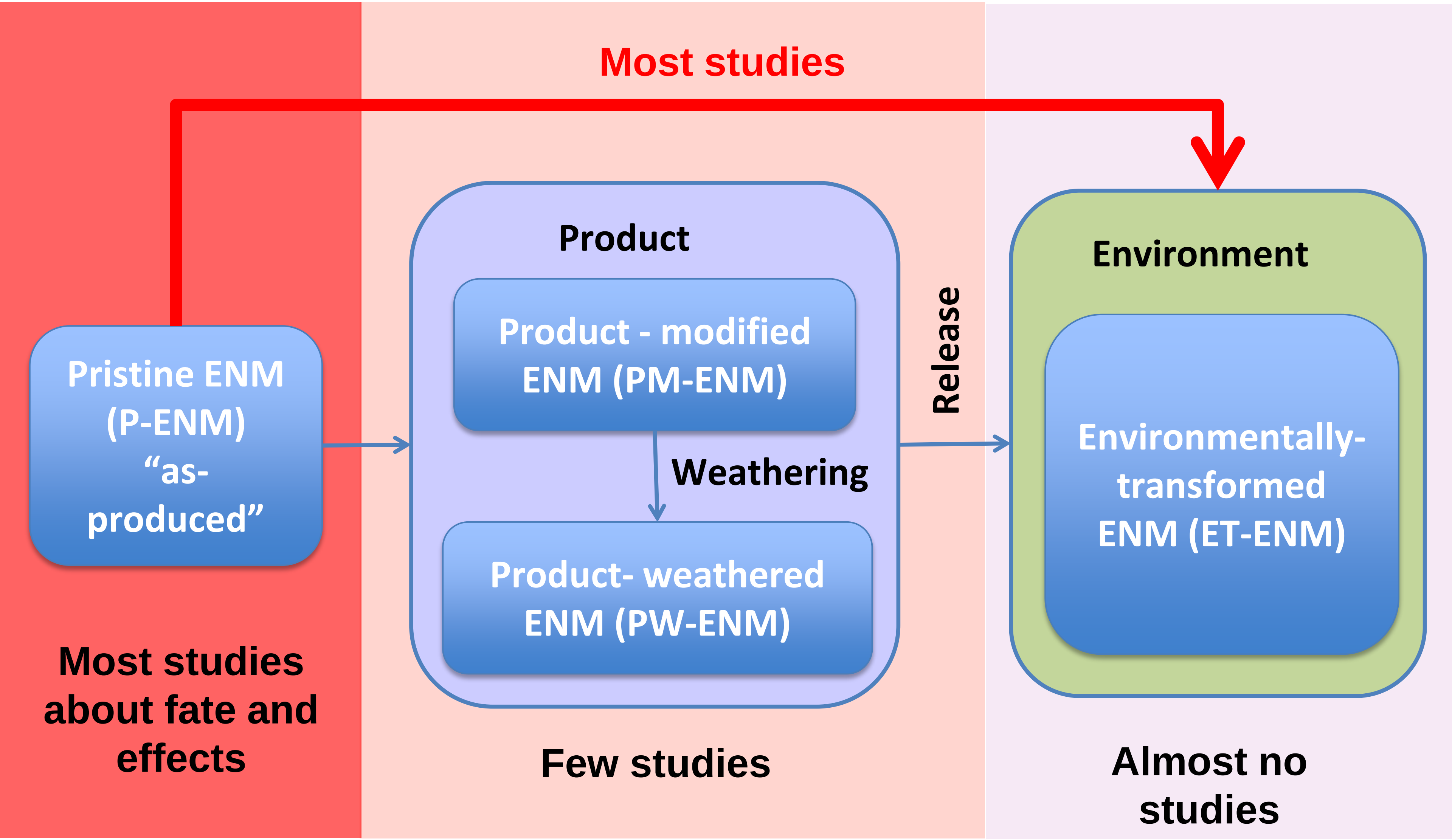
Release and transformation



Modified after Nowack (2012) Environ. Toxicol. Chem. 31: 50-59.

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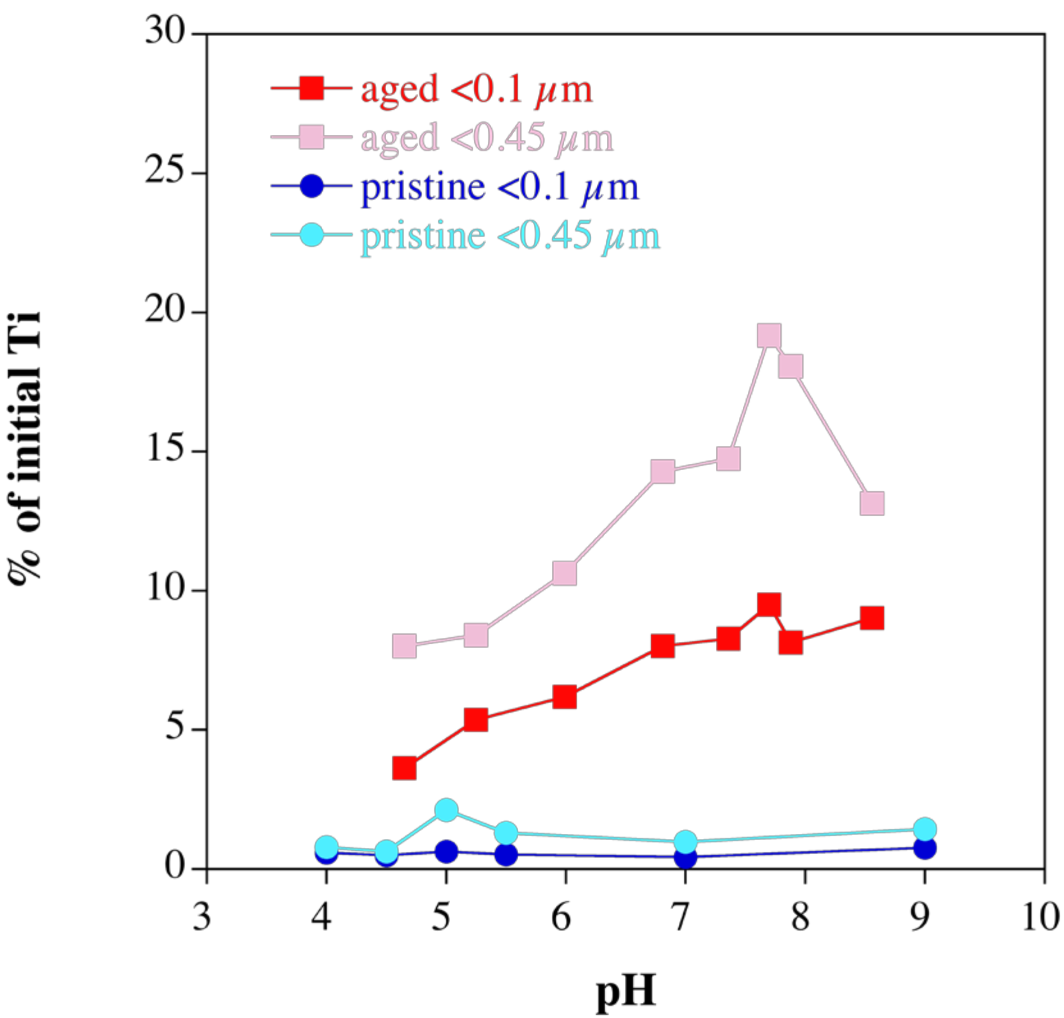
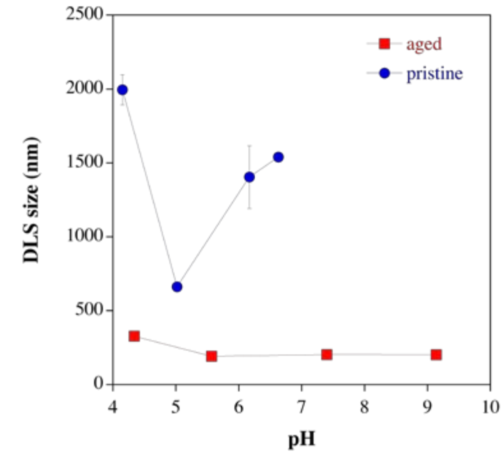
Environmental behavior of released TiO_2

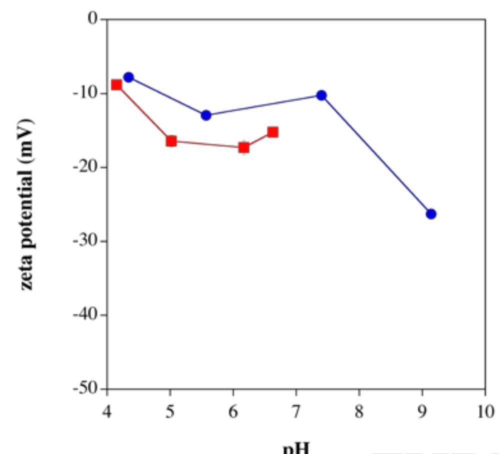
Stability of released TiO_2 in 1 mM Ca, compared to pristine TiO_2



Particle size



Zeta potential



Al-Kattan et al., (2014) *Environ. Sci. Technol.*, 48: 6710−6718

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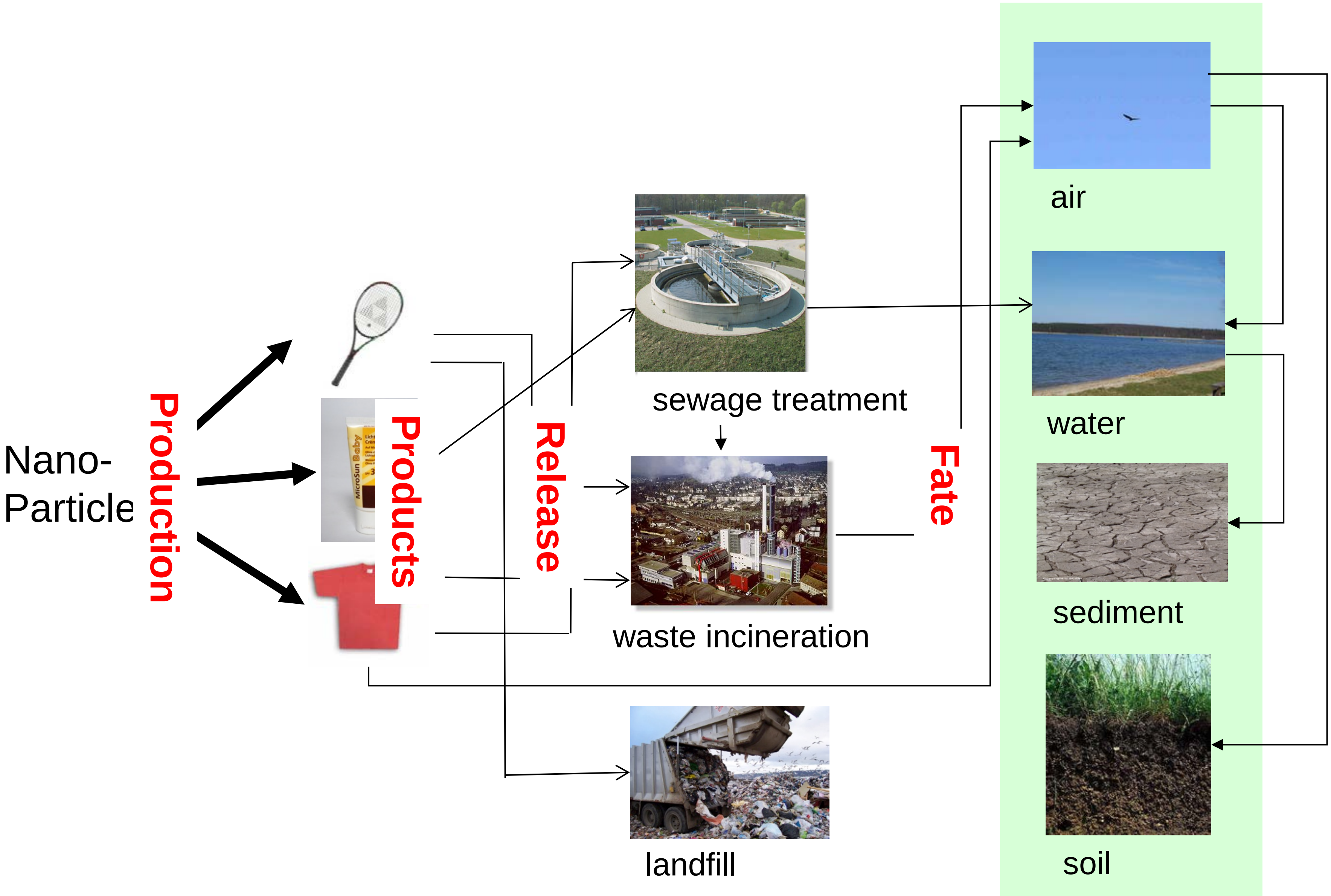
Modeling environmental concentrations



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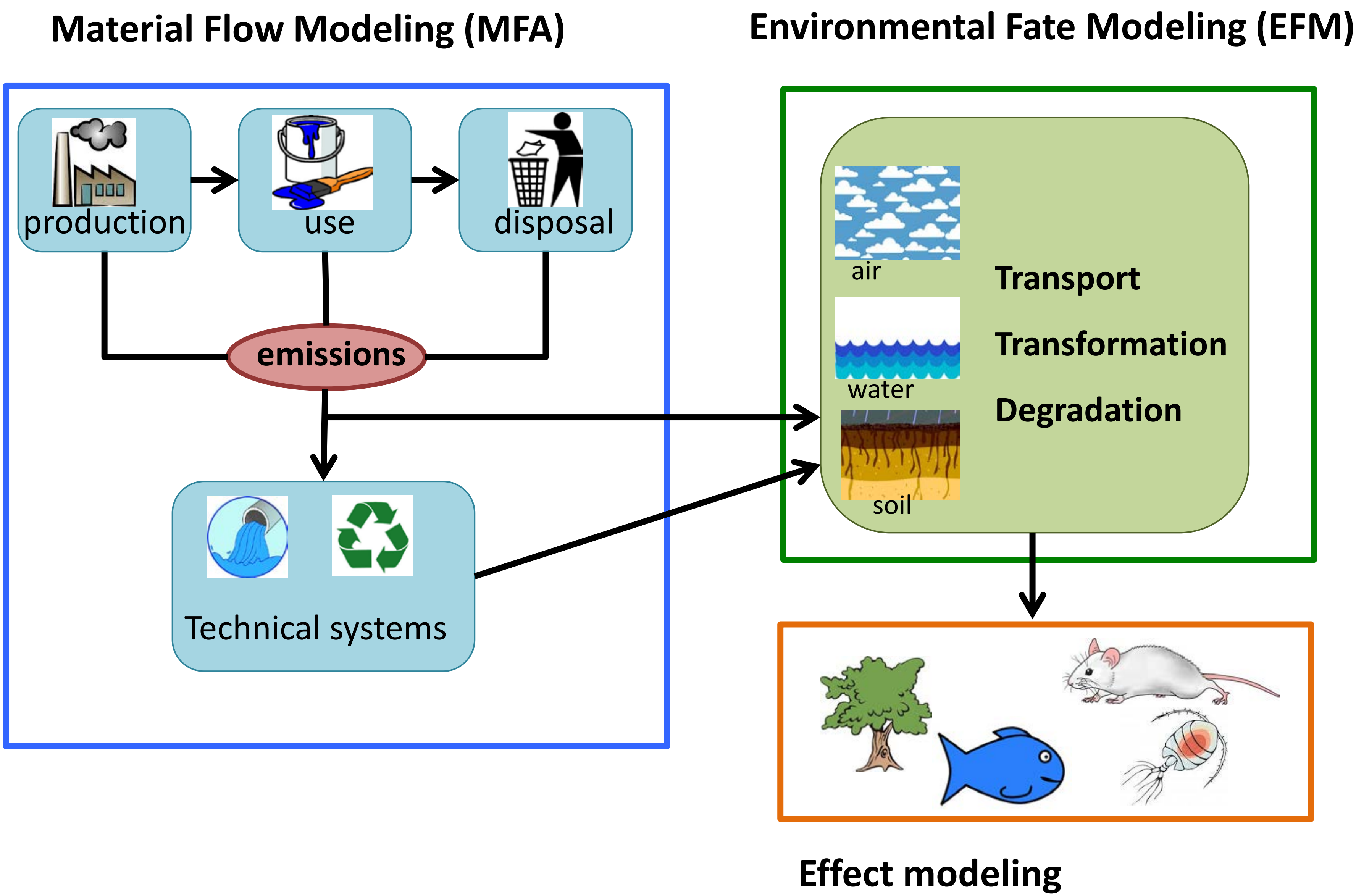
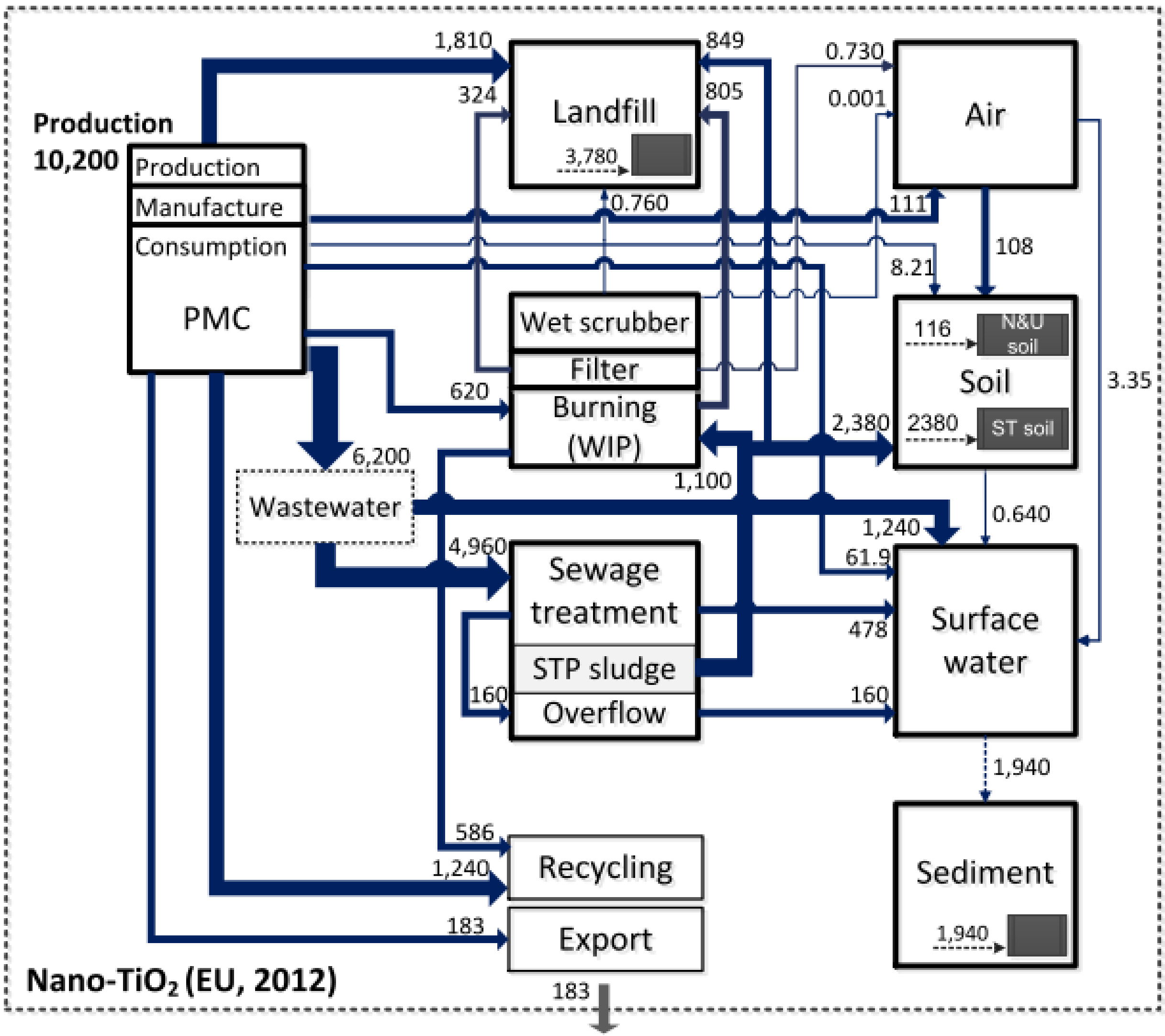
General concept of exposure models



Material-flow model for nano-TiO_2 in the EU

(mode values in tons/year)



Sun et al., (2014) Environ. Pollut. 185: 69-76

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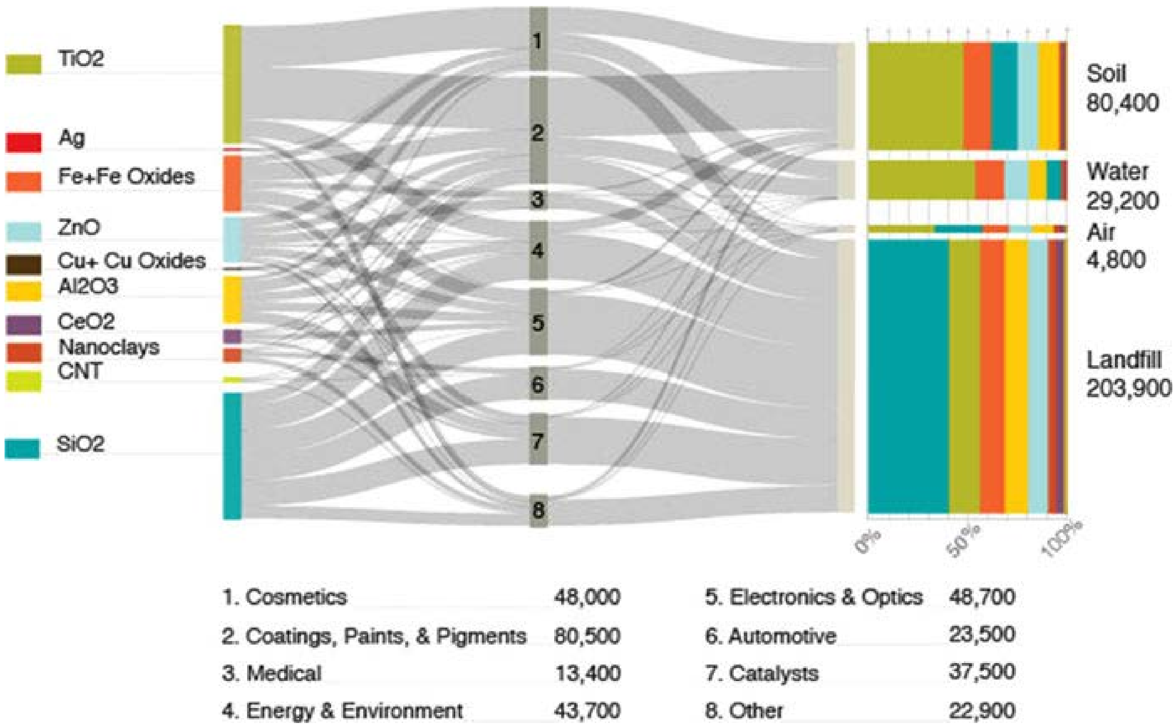
Global Flows



- Source: one market research report
- No uncertainty considered
- Very simple transfer factors
- No transformation

TiO_2

Keller et al. (2013)
J. Nanopart. Res. 15: 1692

From flows to concentrations

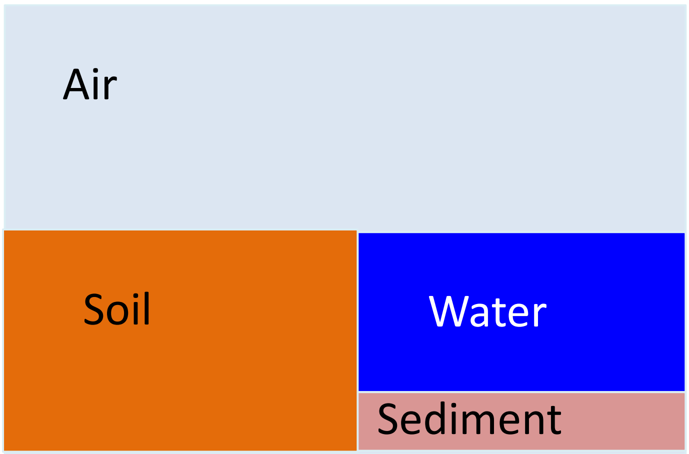


Table R.16-12: Proposed model parameters for regional model

- Well mixed compartments
- Standard volumes assumed
- Source: REACH guidance

Guidance on information requirements and chemical safety assessment Chapter R.16: Environmental Exposure Estimation, ECHA, 2010

Environmental exposure

Example nano-TiO_2

	EU			
	Mode	**$Q_{0.15}$**	**$Q_{0.85}$**	
STP Effluent	16	13	110	µg/L
Surface water	0.53	0.40	1.4	µg/L
Sediment	1.9	1.4	4.8	mg/kg·y
STP sludge	170	150	540	mg/kg
Natural and urban soil	0.13	0.09	0.24	µg/kg·y
Sludge treated soil	1200	940	3600	µg/kg·y
Air	0.001	0.000	0.001	$\mu g/m^3$
Solid waste	12	8.3	20	mg/kg
WIP bottom ash	120	82	230	mg/kg
WIP fly ash	150	110	310	mg/kg

Sun et al., (2014) Environ. Pollut. 185: 69-76

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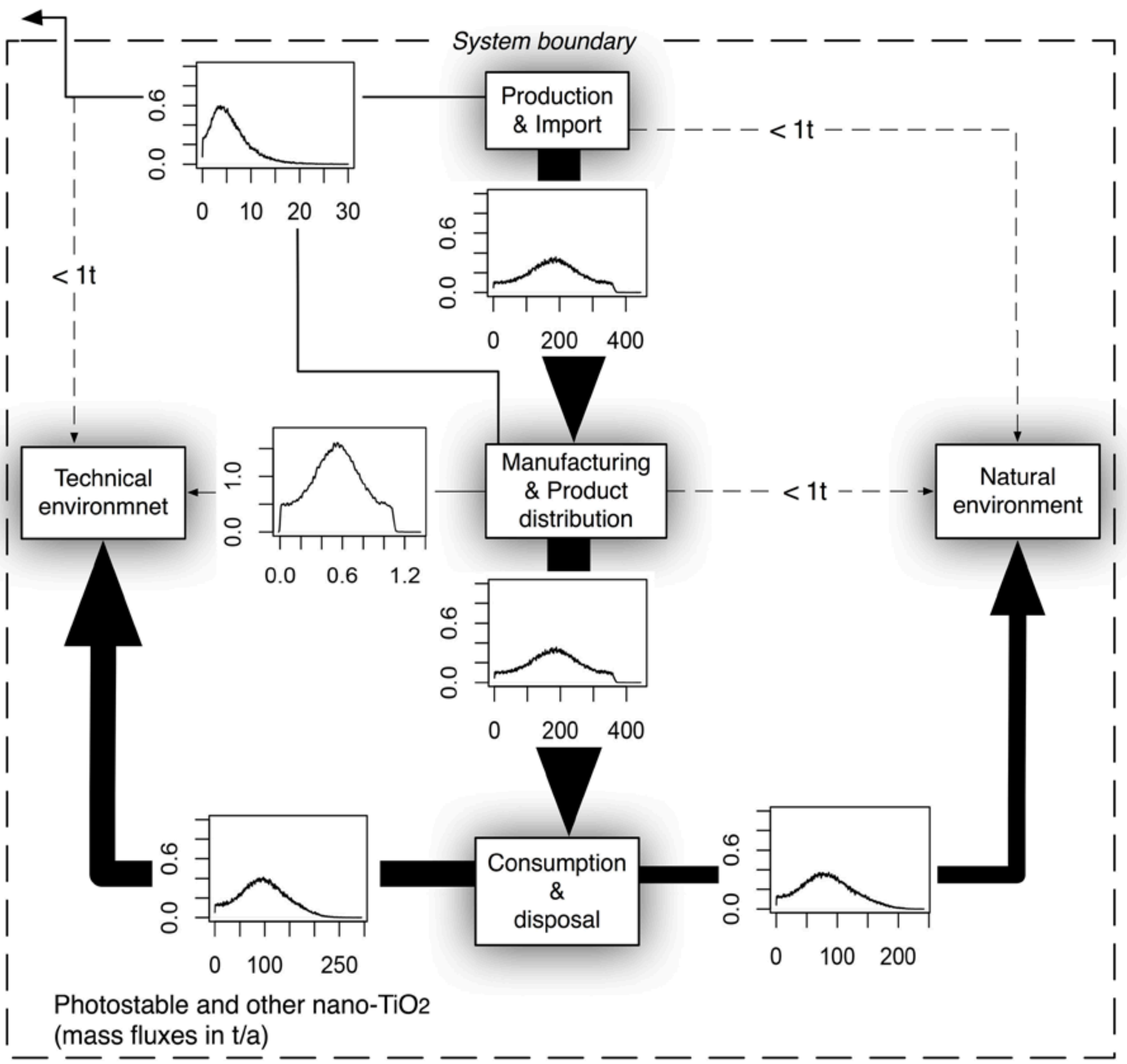
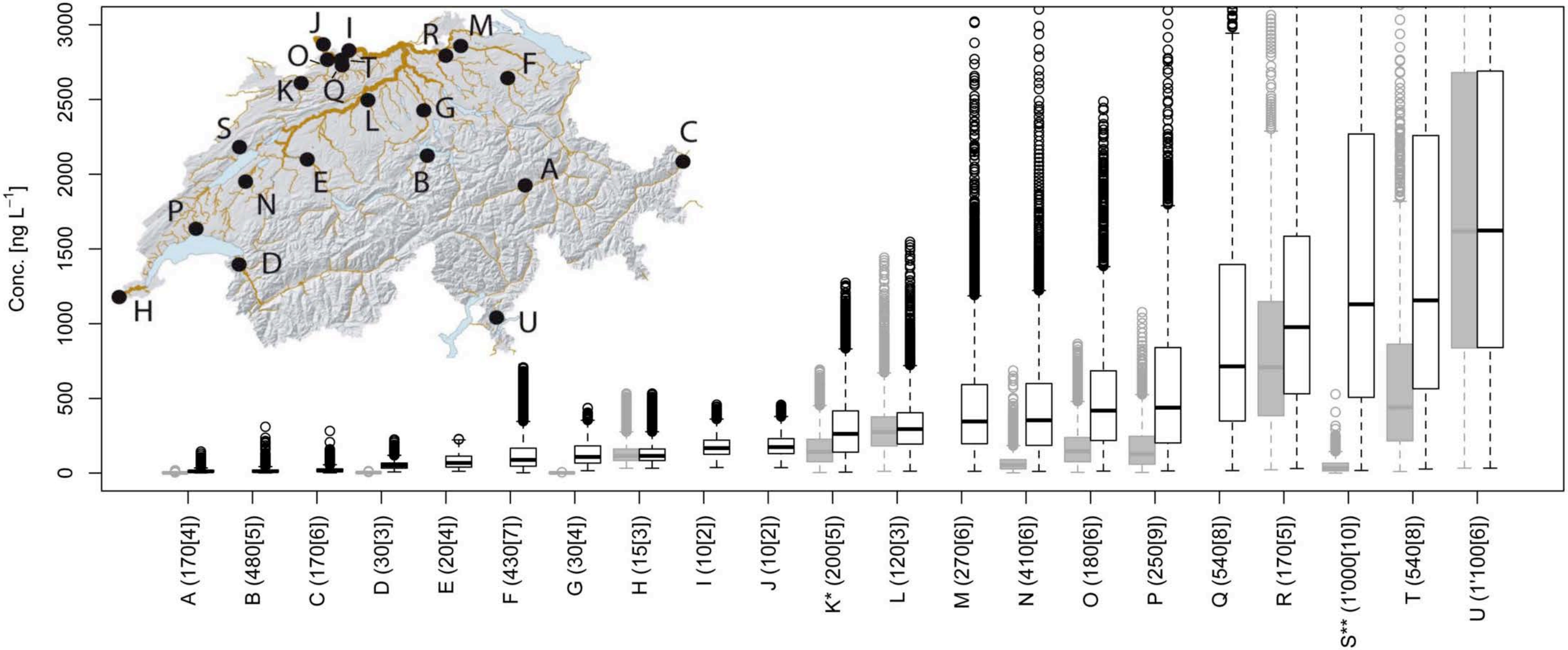
Probabilistic modeling



Gottschalk et al., (2015) *Int. J. Environ. Res. Public Health* 12: 5581-5602.

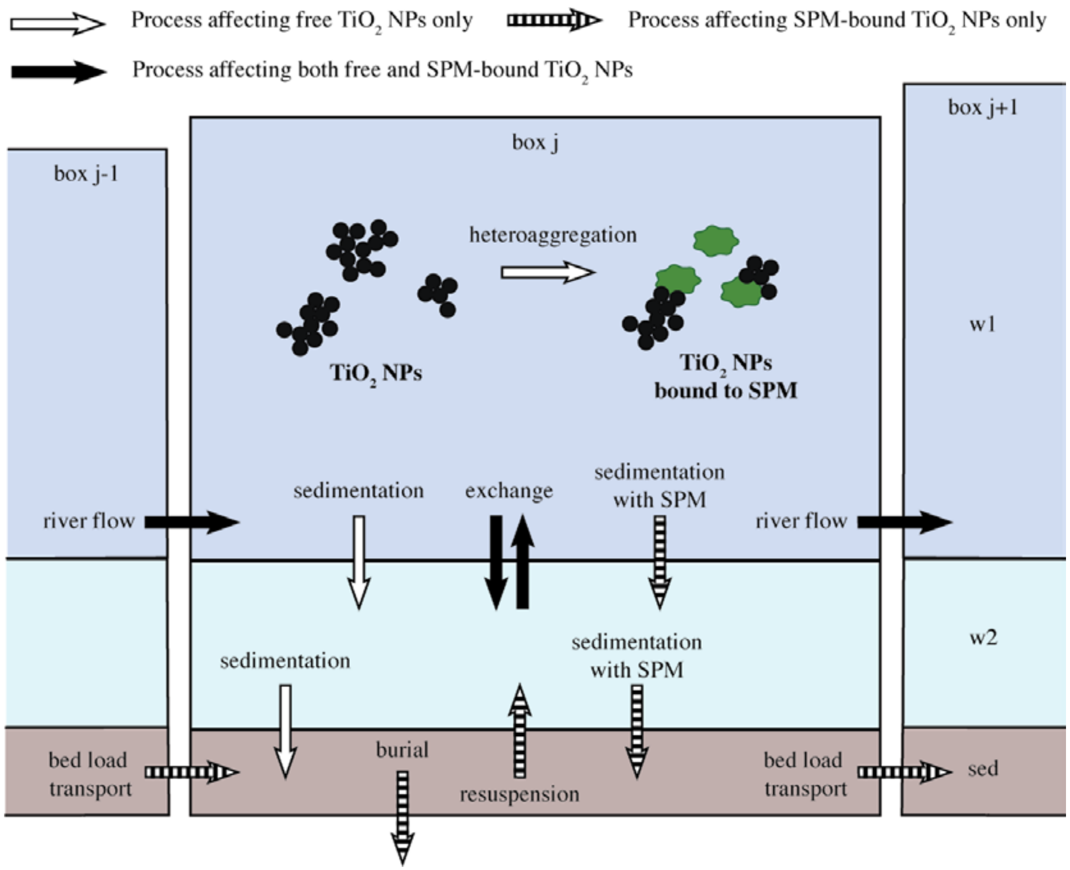
Geographic variability

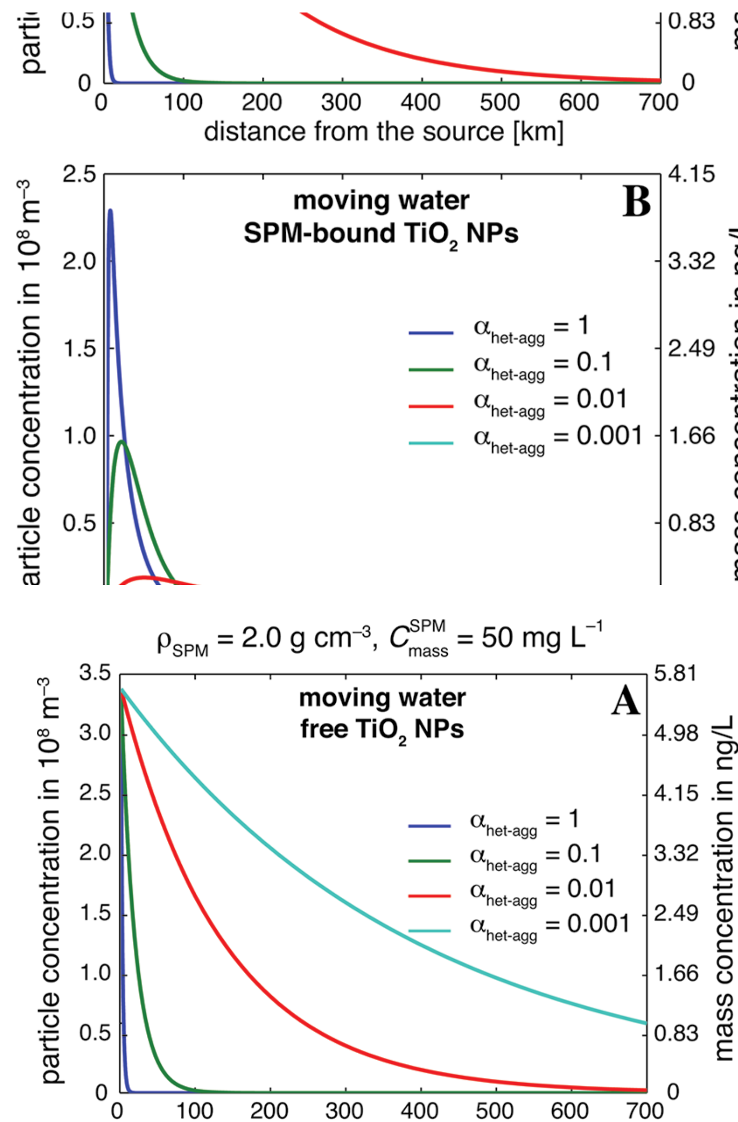
Nano-TiO_2 based on 20-year flow data



Gottschalk et al., (2011) *Environ. Pollut.* 159: 3439-3445

Environmental fate modeling: Rivers





Praetorius (2012) Environ. Sci. Technol. 46: 6705-6713

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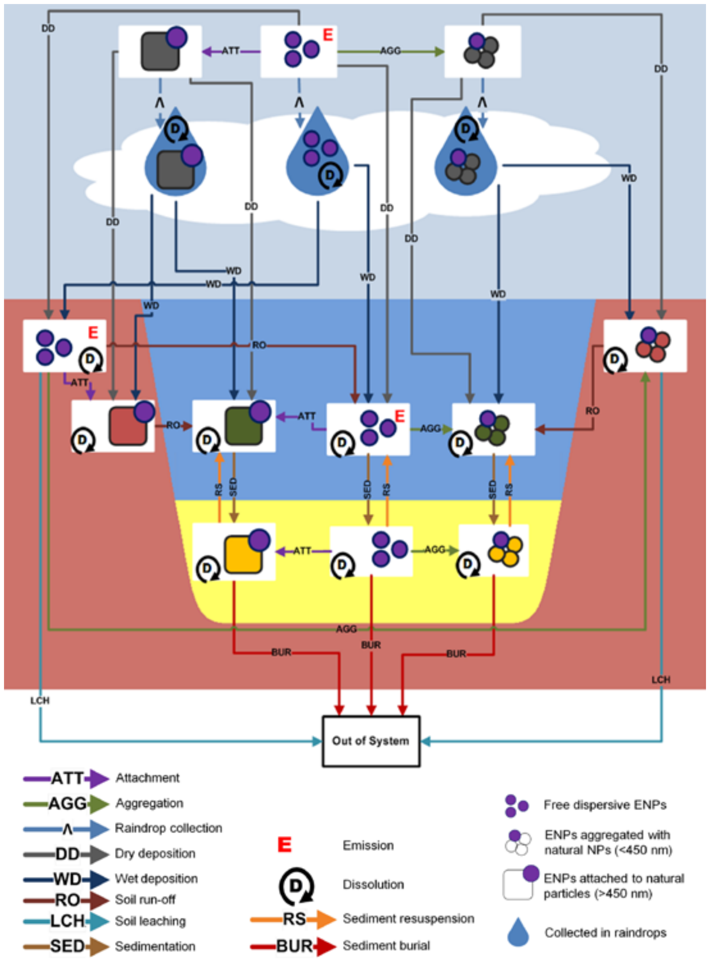
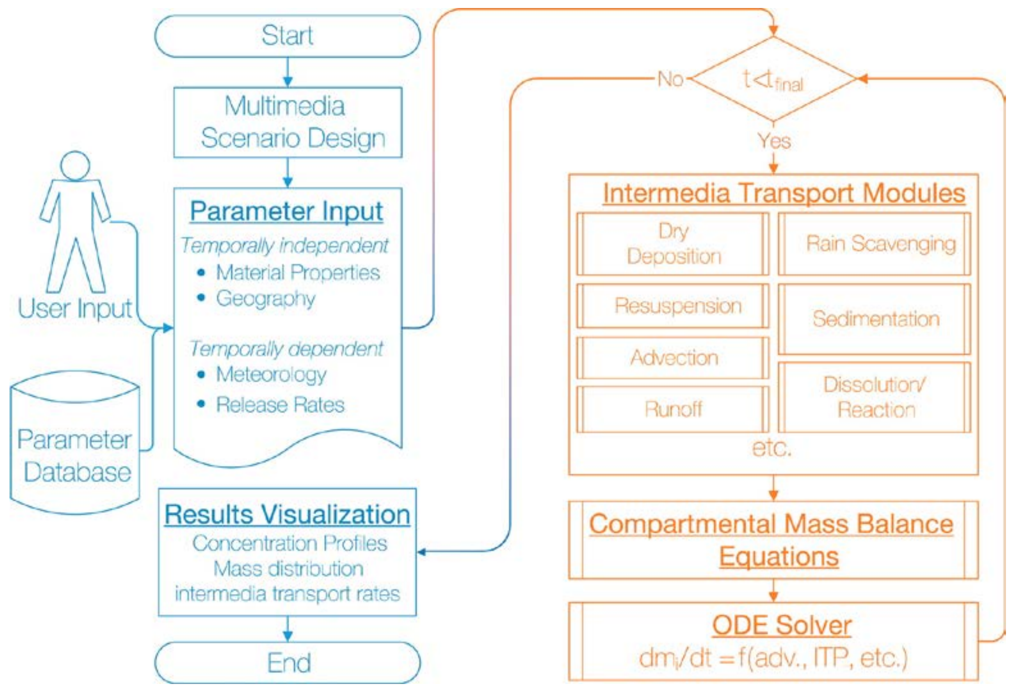
Complete environmental fate modeling

SimpleBox4Nano



MendNano



Meesters et al. (2014) Environ. Sci. Technol. 48, 5726−5736

Liu and Cohen (2014) Environ. Sci. Technol. 48, 3281-3292.

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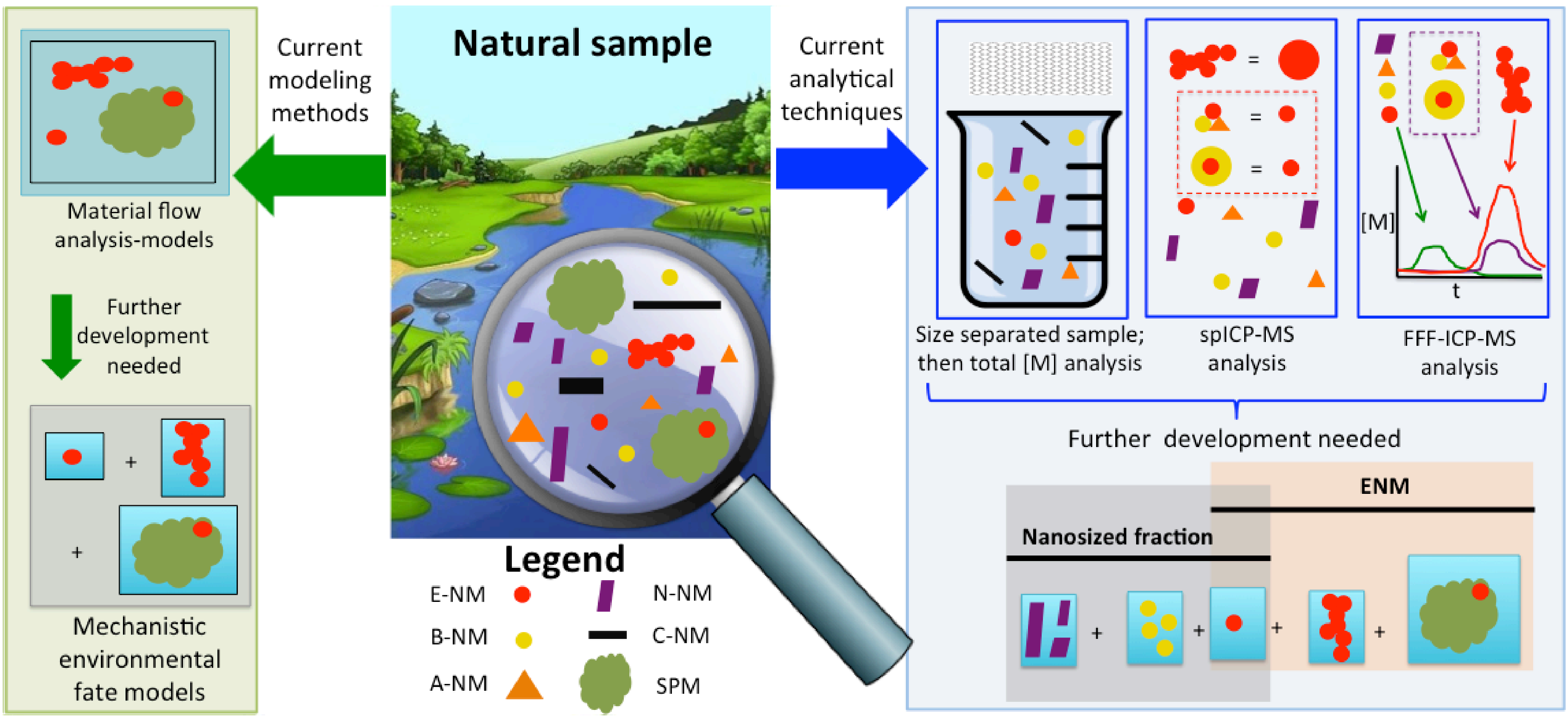
Coupled MFA and fate model

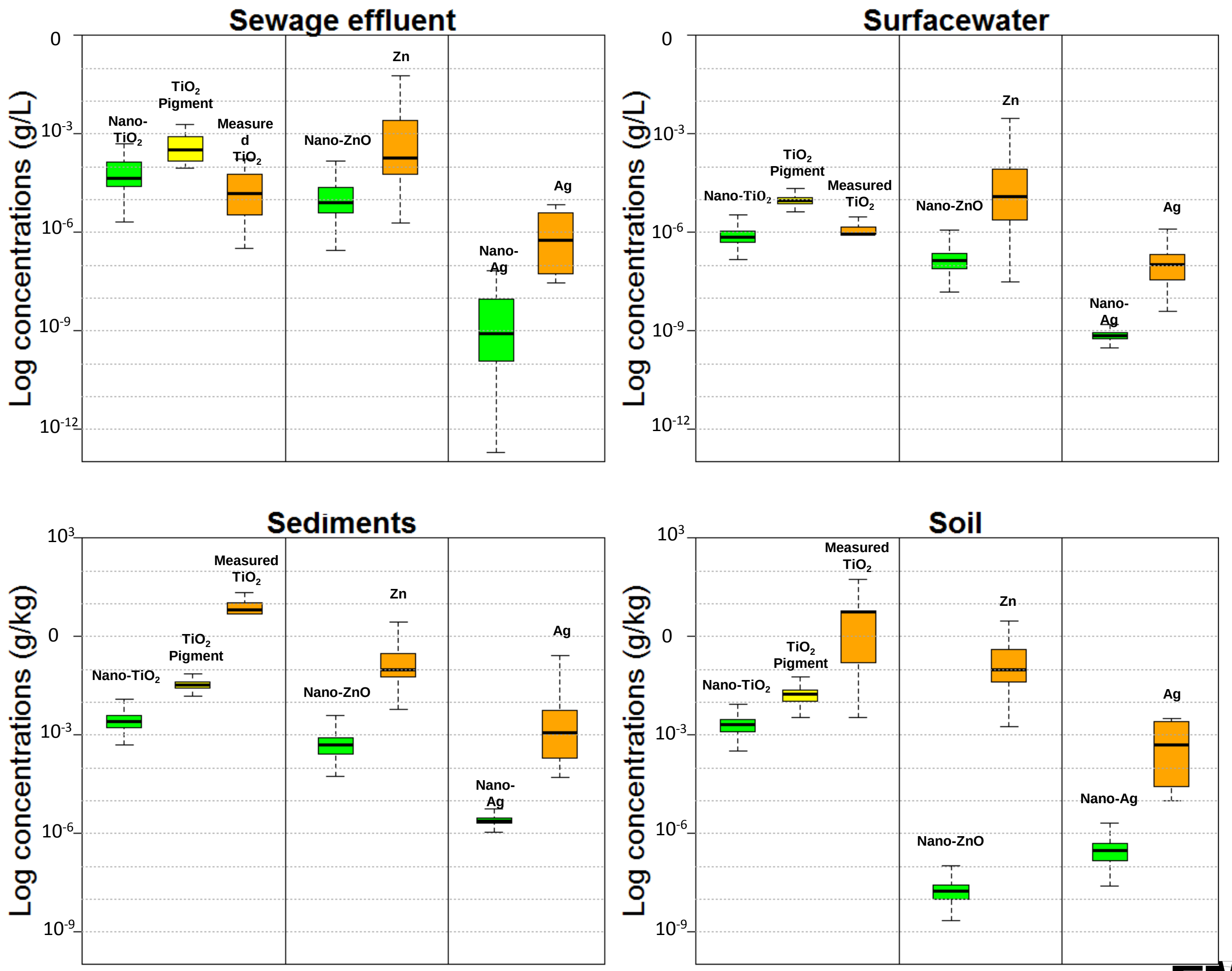
Praetorius et al., (2015)
Env. Sci: PI submitted

Validation



Nowack et al., Environ. Sci. Nano, submitted

Comparison nano and conventional metals



Sun et al., (2014) Environ. Pollut. 185: 69-76

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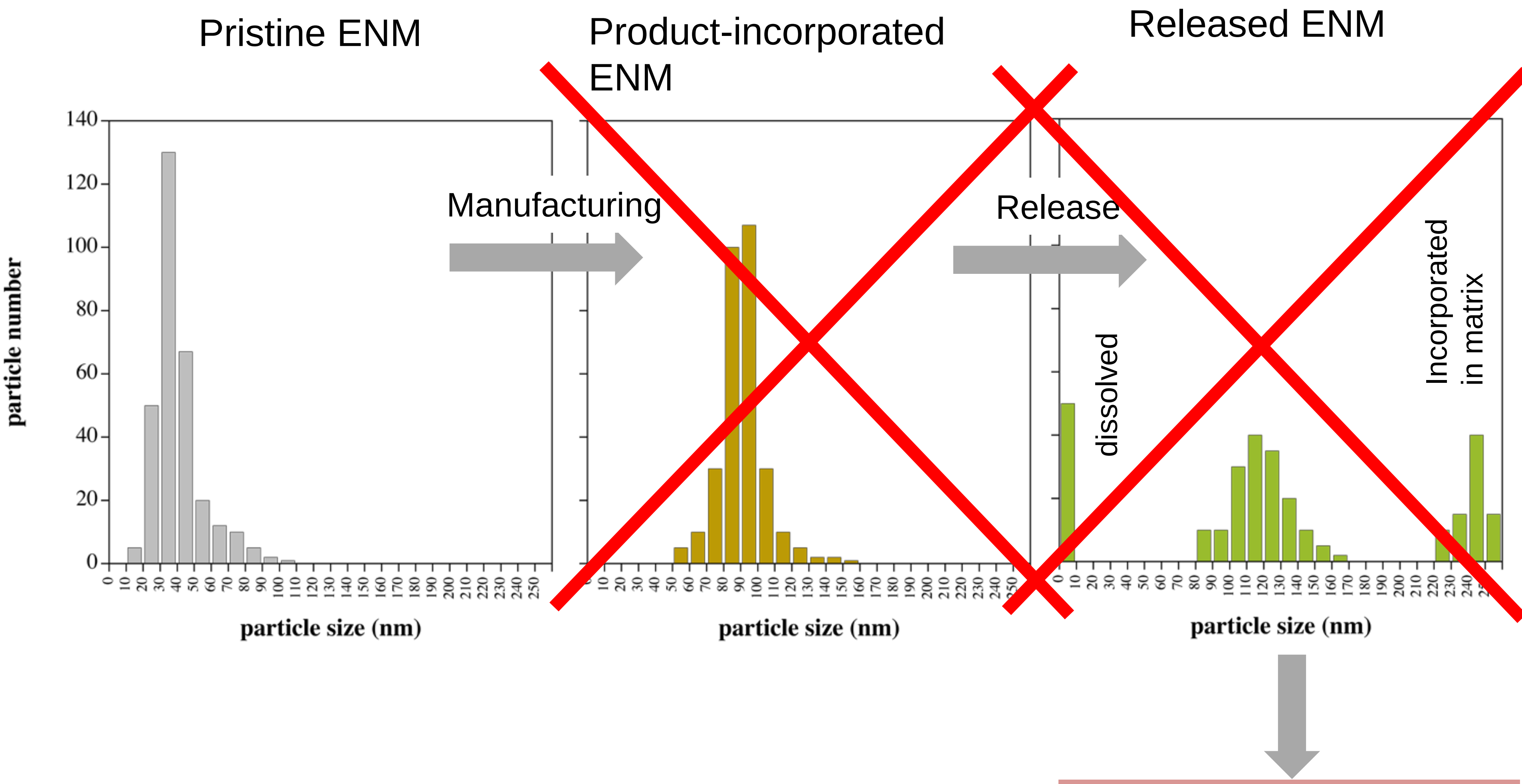
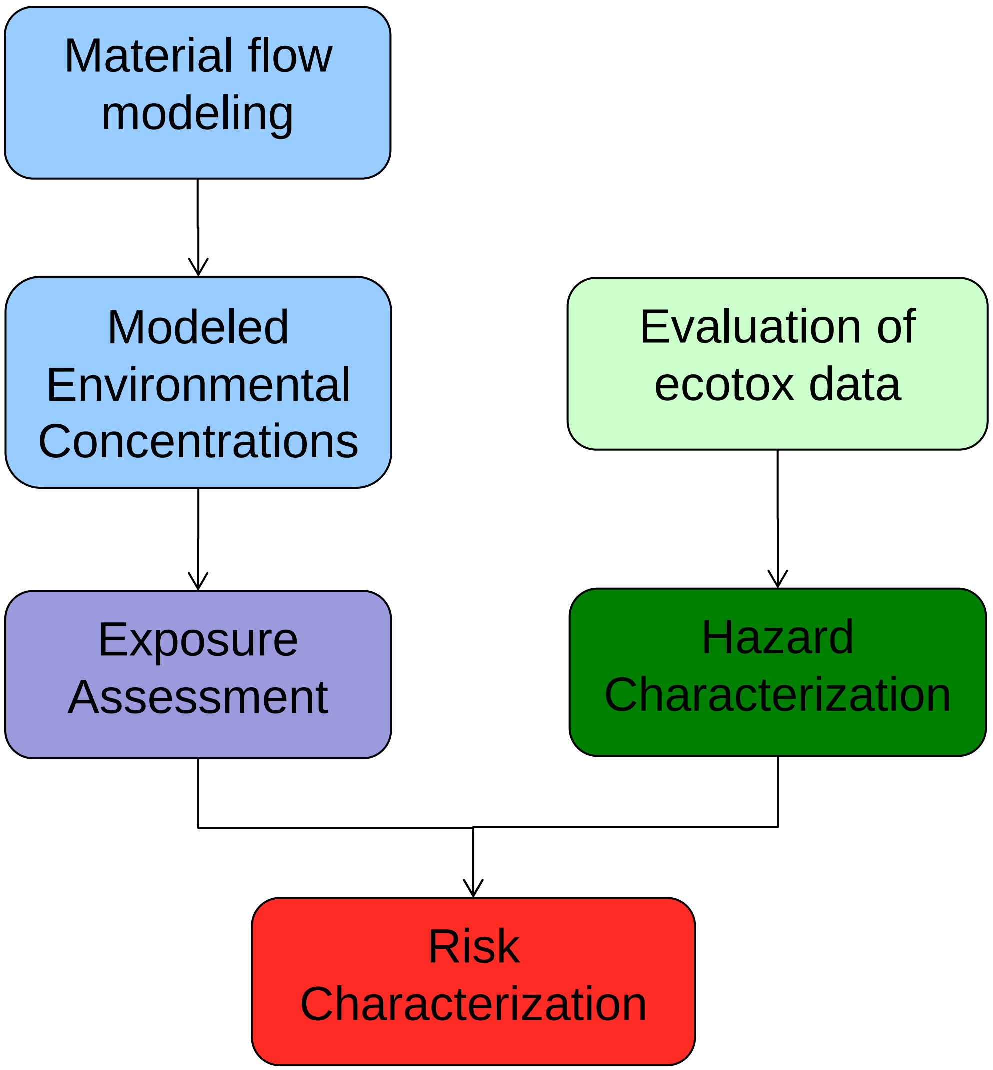
Needs for fate modeling



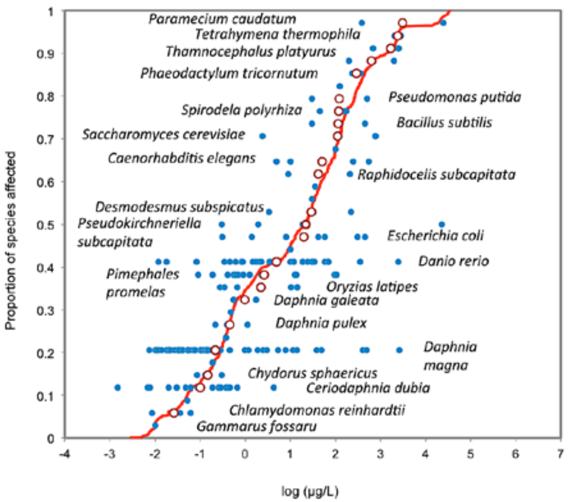
Needed in environmental fate models

Risk Characterization of ENM

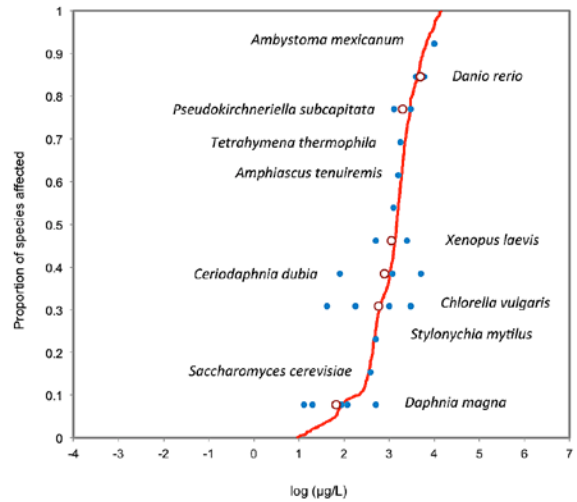


Hazard characterization (freshwater)

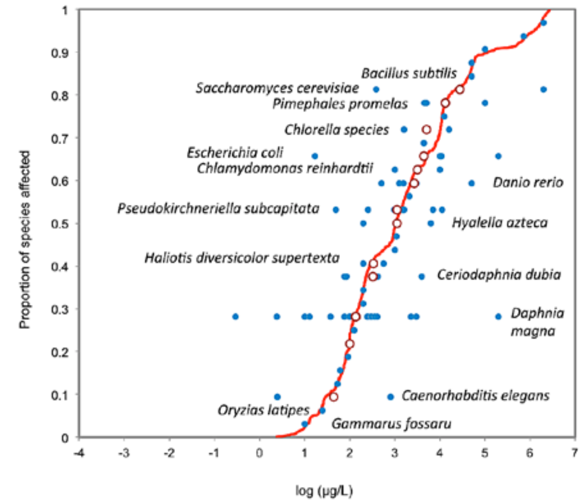
Nano-Ag



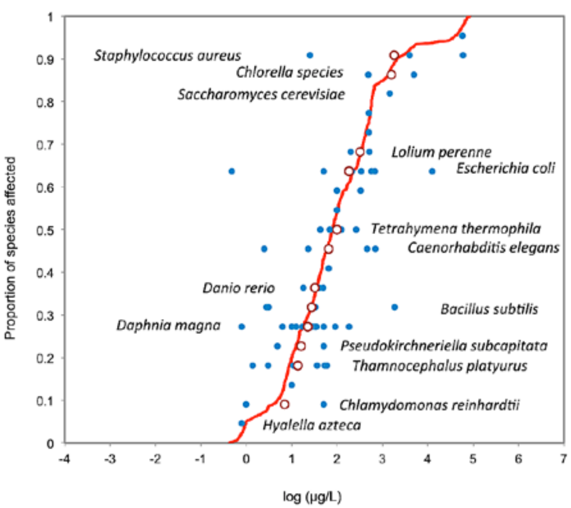
CNT



Nano-TiO_2



Nano-ZnO



- Species sensitivity distributions (SSD)
- State: 2014
- Available for water, soil, (sediment)
- Used to derive PNEC from HC5

Coll et al., Nanotoxicology, revised version submitted

Gottschalk et al. (2013) Environmental Toxicology and Chemistry 32: 1278–1287

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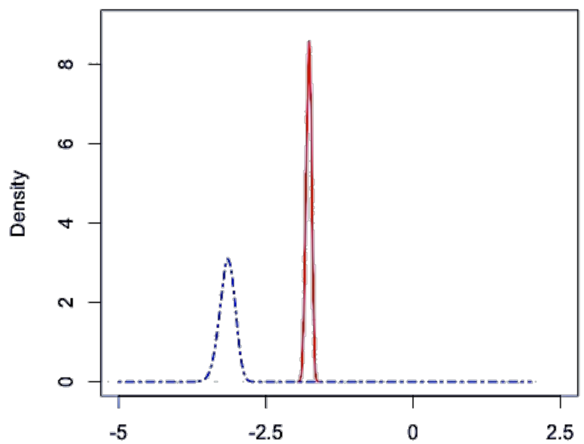
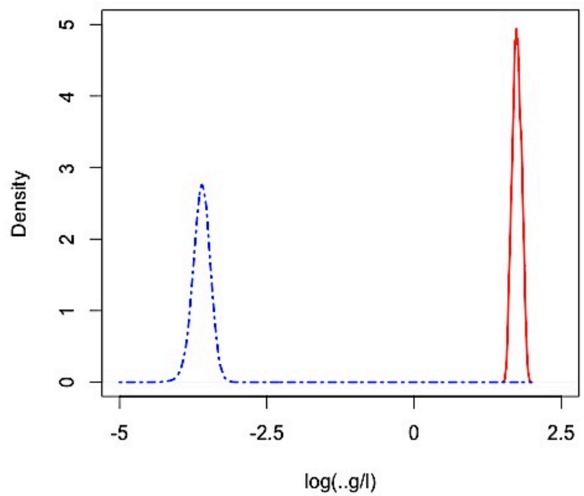
Risk characterization (freshwater)

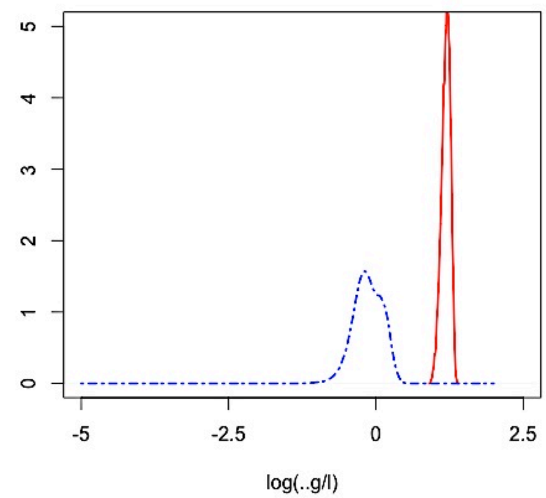
Nano-Ag



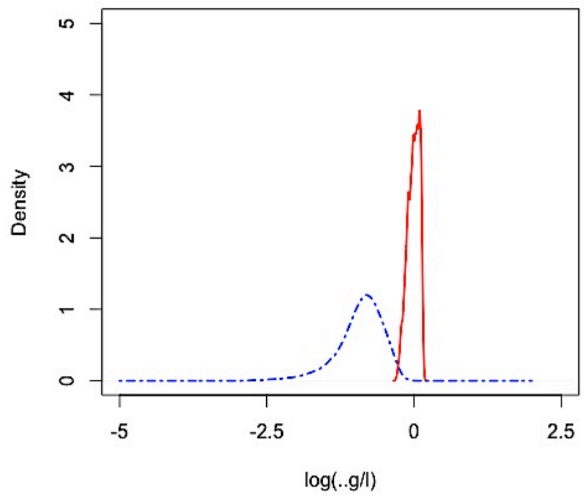
CNT



Nano-TiO_2



Nano-ZnO



- Predicted environmental concentration (PEC) from Sun (2014)
- Predicted no effect concentrations (PNEC) from SSD

Coll et al., Nanotoxicology, revised version submitted

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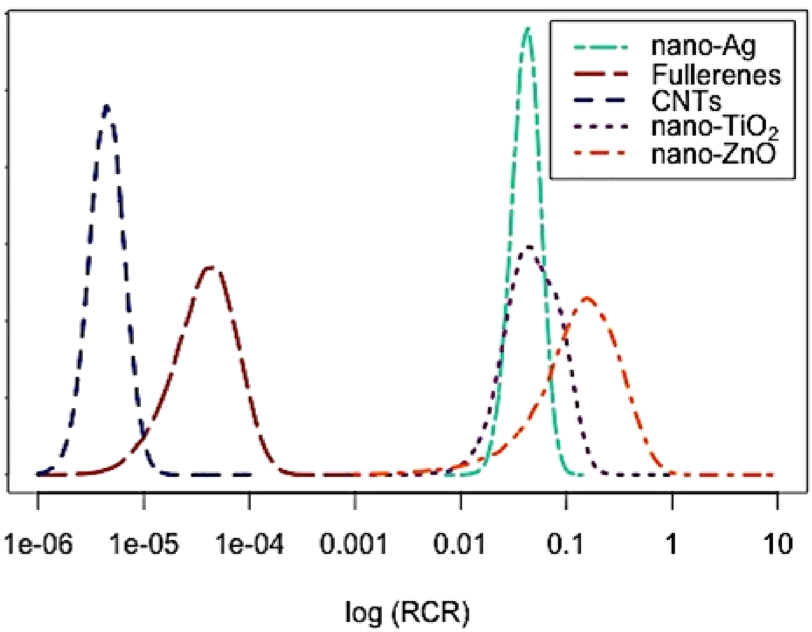
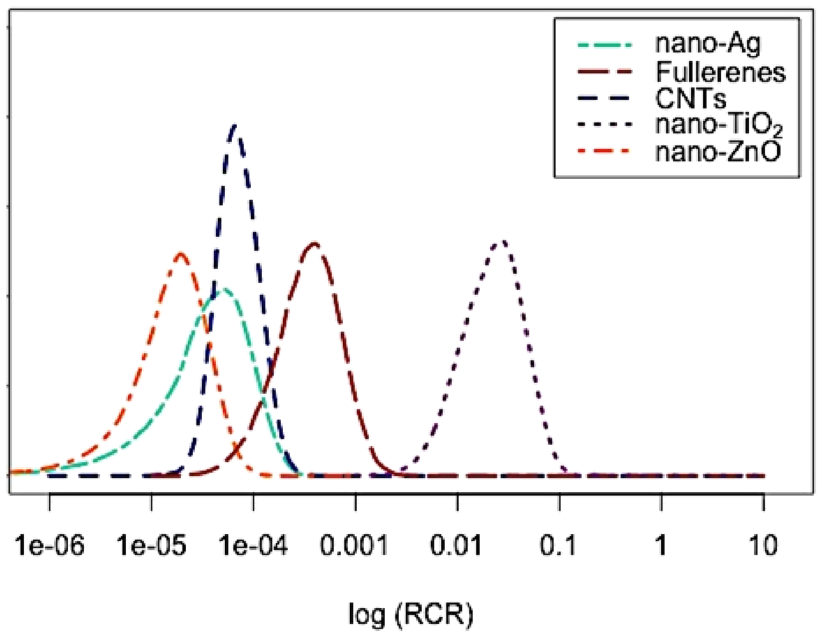
Risk characterization

Freshwater



Soil



Risk Characterization Ratio (RCR) = PEC/PNEC

Coll et al., Nanotoxicology, revised version submitted

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Conclusions

- Life-cycle-based modeling can provide predictions of flows to the environment
- Knowledge about use and release of ENM is scarce
- Release is the link between products and exposure
- Flow data can be converted to environmental concentrations
- Coupling of flow and fate modeling is possible, but size distribution input data are not available
- Validation of modeled data by measurements is not yet possible
- Comparison of exposure concentrations with effect data can be performed

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Thank you for your attention!

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