Nanomaterial Fate and Exposure Research:
Where we are now and where we need to be to model environmental exposures

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CEINT Center for the Environmental Implications of NanoTechnology
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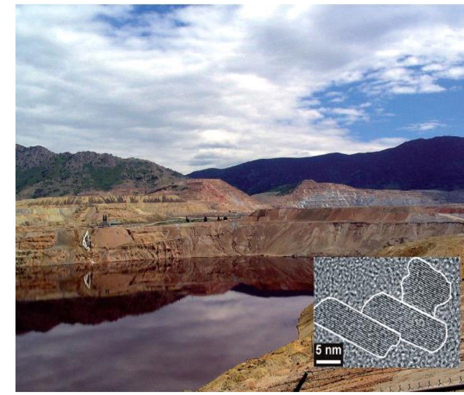
Environmental Fate Modeling

NM Sources/Inputs

Environmental Processing

Where are the NMs?
What is their form?
What are the NMs doing?



Exposure Route 1

Exposure Route 2

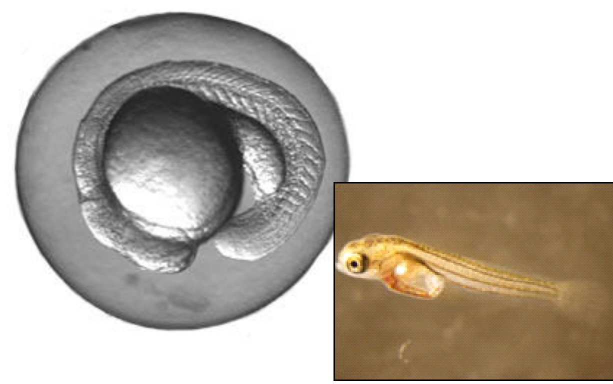
Exposure Route 3

Effects of Interest

Acute Toxicity

Chronic/Multigenerational Effects

Ecosystem Function/Services



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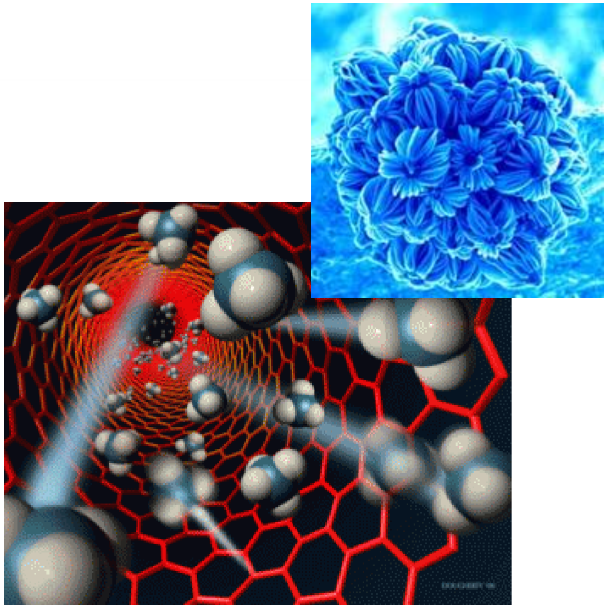
In the Beginning……

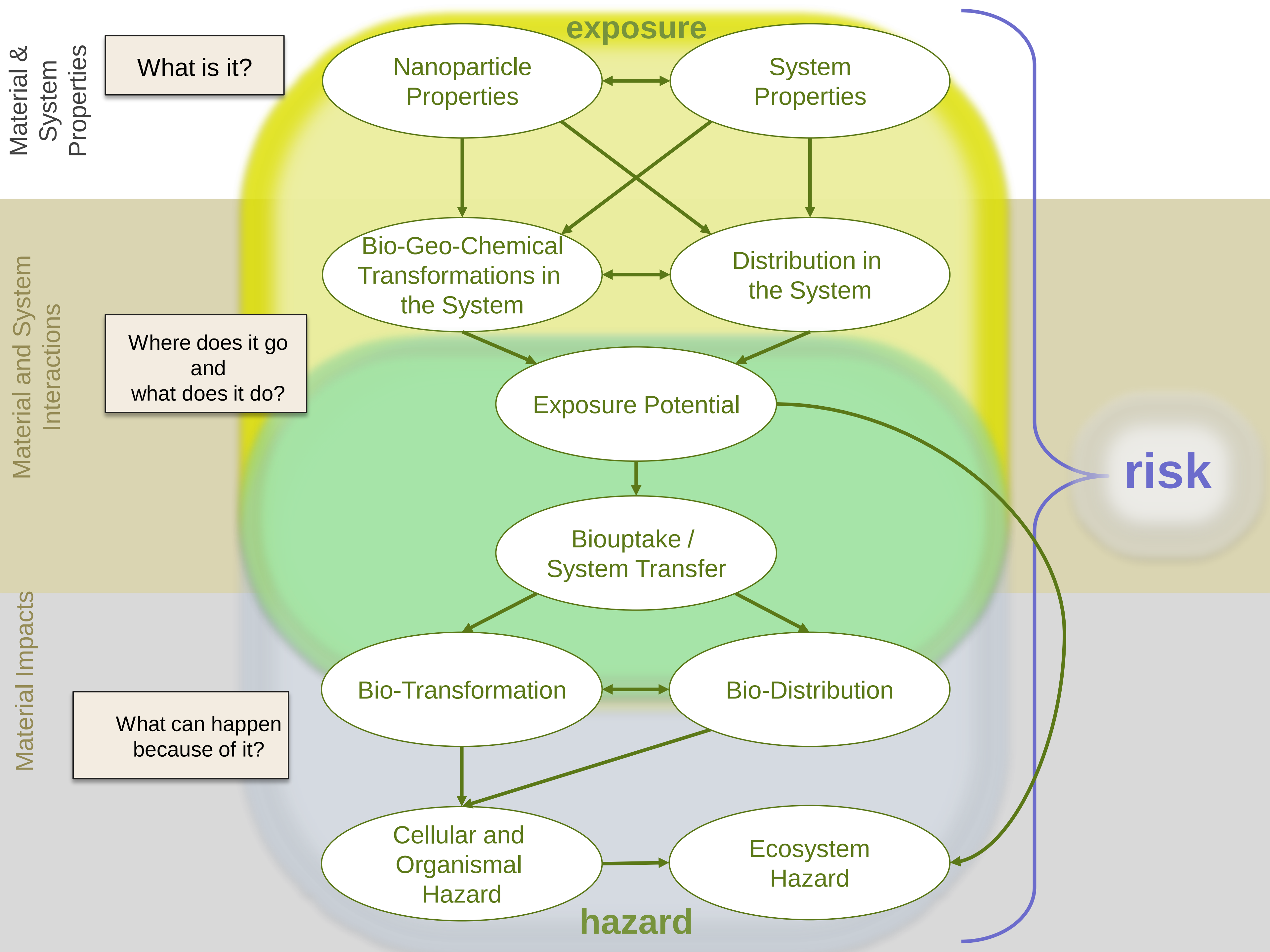
What is it?

Nanomaterial Descriptors

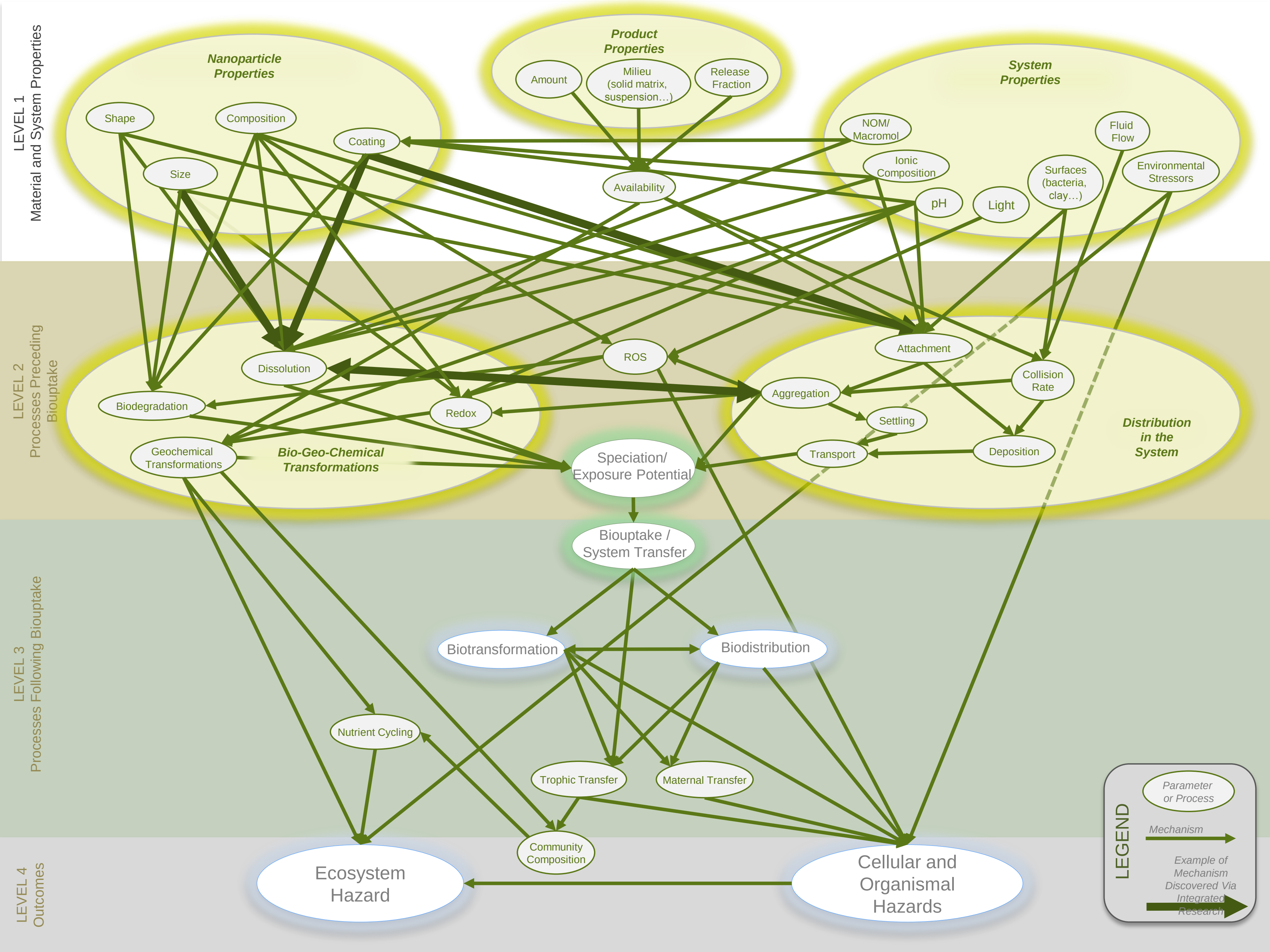


What can happen because of it?

Nanoparticle Impacts



Material & System Properties
What is it?
exposure
Nanoparticle Properties
System Properties
Bio-Geo-Chemical Transformations in the System
Distribution in the System
Material and System Interactions
Where does it go and what does it do?
Exposure Potential
Biouptake / System Transfer
risk
Material Impacts
Bio-Transformation
Bio-Distribution
What can happen because of it?
Cellular and Organismal Hazard
Ecosystem Hazard
hazard

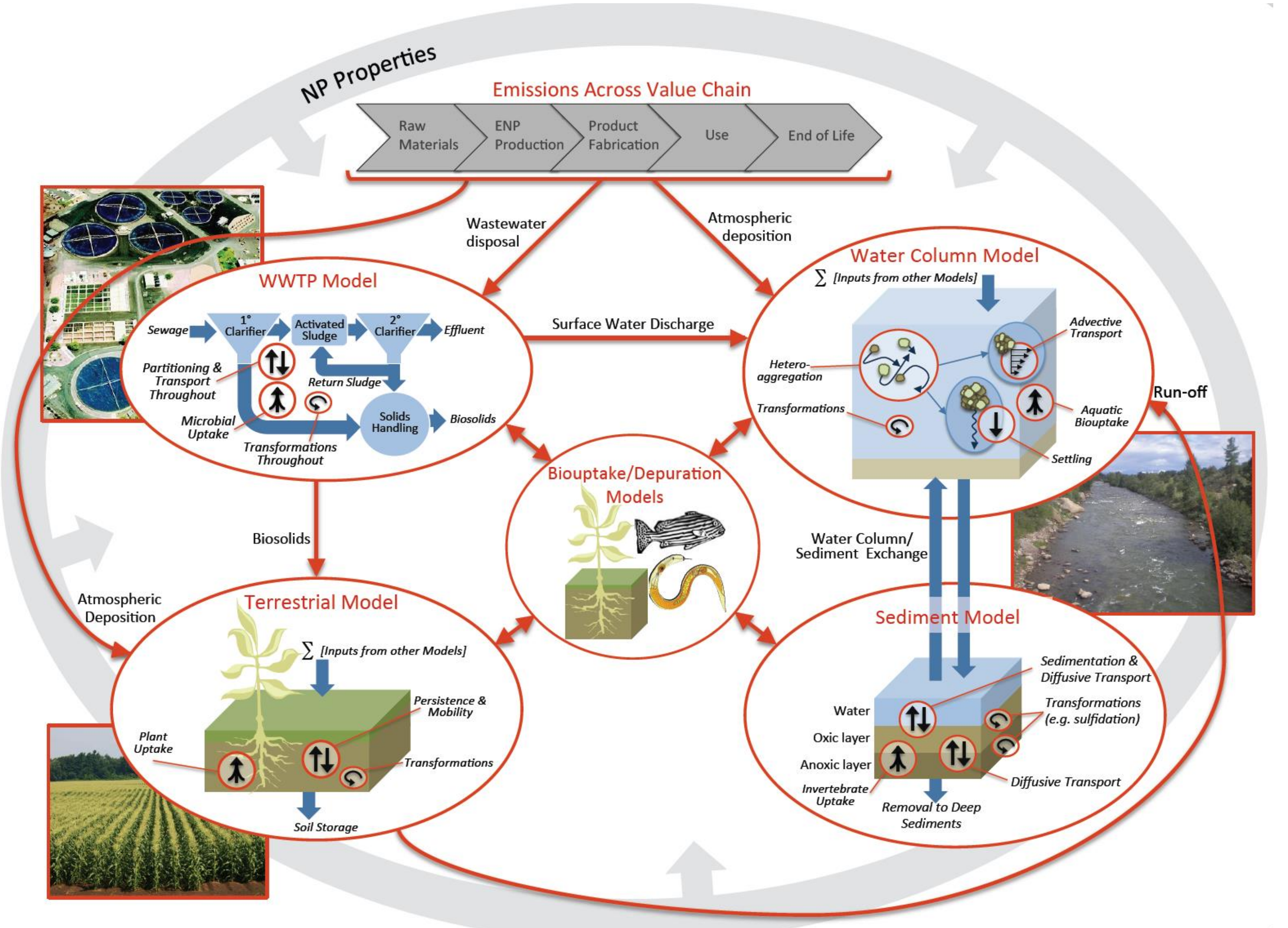


LEVEL 1
Material and System Properties
Nanoparticle Properties
Shape
Composition
Coating
Size
Product Properties
Amount
Milieu (solid matrix, suspension…)
Release Fraction
Availability
System Properties
NOM/ Macromol
Ionic Composition
pH
Light
Surfaces (bacteria, clay…)
Fluid Flow
Environmental Stressors
LEVEL 2
Processes Preceding Biouptake
Dissolution
Biodegradation
Redox
ROS
Geochemical Transformations
Bio-Geo-Chemical Transformations
Speciation/ Exposure Potential
Attachment
Collision Rate
Aggregation
Settling
Transport
Deposition
Distribution in the System
Biouptake / System Transfer
LEVEL 3
Processes Following Biouptake
Biotransformation
Biodistribution
Nutrient Cycling
Trophic Transfer
Maternal Transfer
Community Composition
LEVEL 4
Outcomes
Ecosystem Hazard
Cellular and Organismal Hazards
LEGEND
Parameter or Process
Mechanism
Example of Mechanism Discovered Via Integrated Research

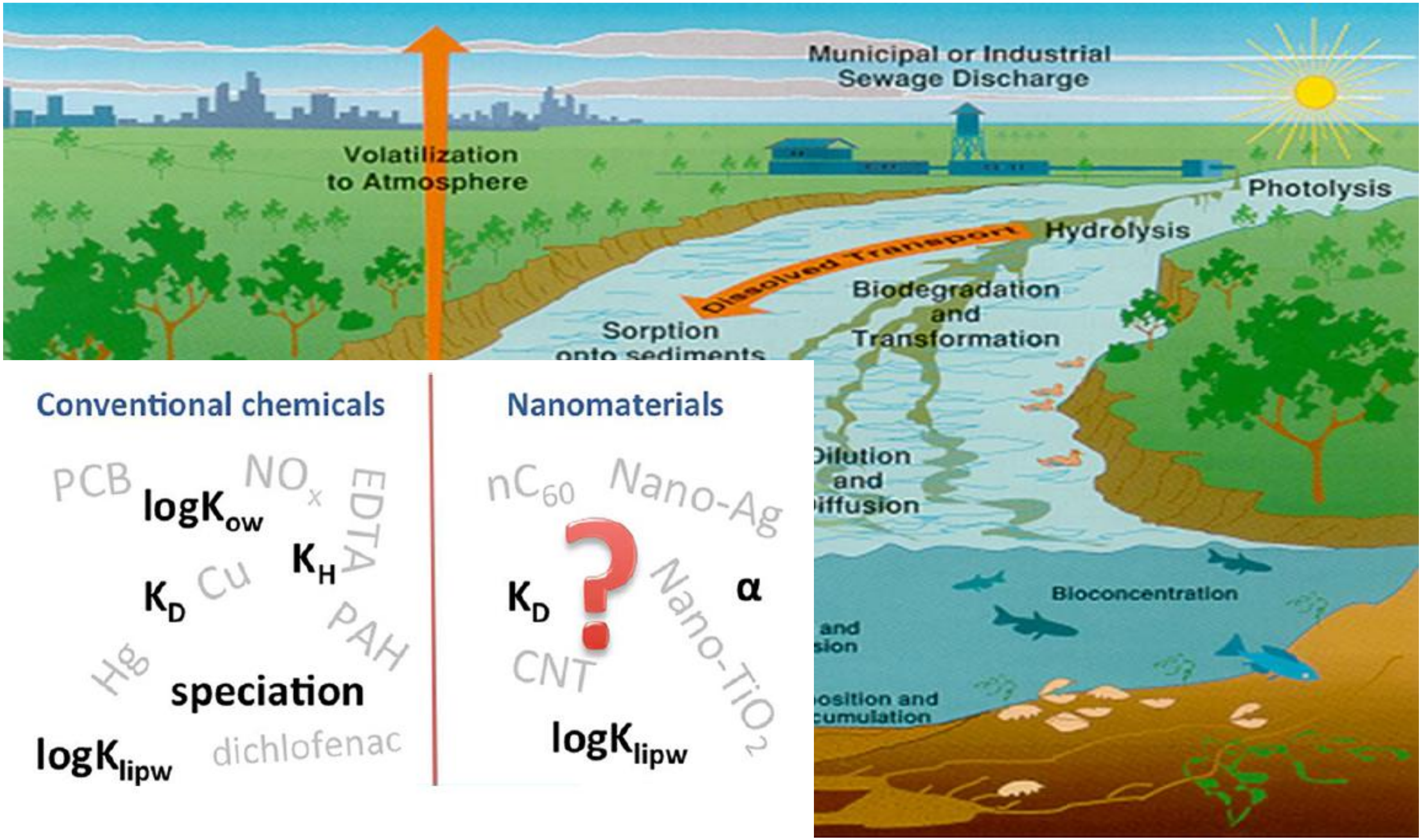
Key Questions to Address?

- What models, systems, and model frameworks do we need?
- What are the key parameters and inputs needed in those models?
- How do we measure those parameters for nanomaterials in complex systems?
- How can we validate our models?

Some Key Models are Required



What Model Parameters Best Describe Fate?



Meade (ed.) USGS Circular 1133, 1995

Westerhoff and Nowack, 2013, Accounts in Chemical Research 46: 844-853.

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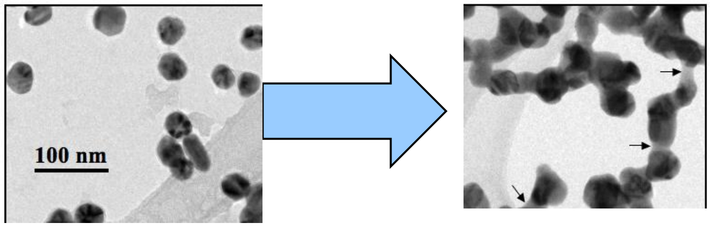
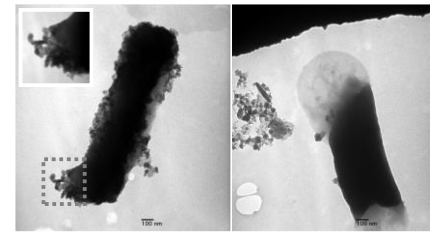
Most Fate Work Can *Inform* Models, but cannot *Parameterize* the Models

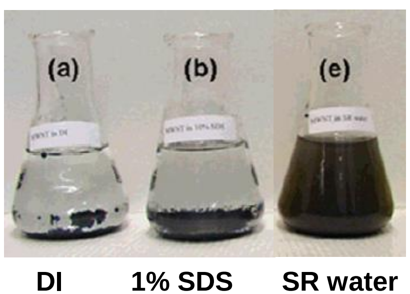
Ag



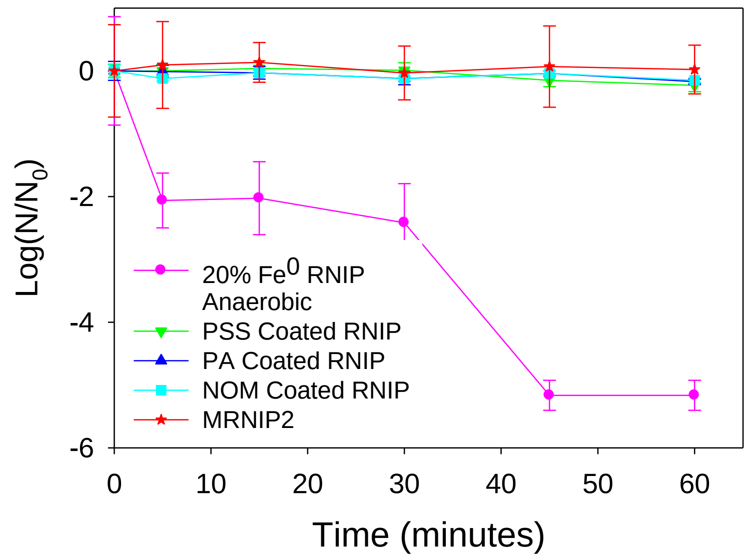
Ag_2S



Levard et al., ES&T 2011 45 (12), 5260.
Ma et al., 2013 ES&T 47 (6), pp 2527–2534;
Ma et al., 2014 ES Nano 1 347-357.



Hyung, et al. *Environ. Sci. Technol*. 2006 41(1) 179-184



Li et al., *ES&T* 44 (9) 3462-346

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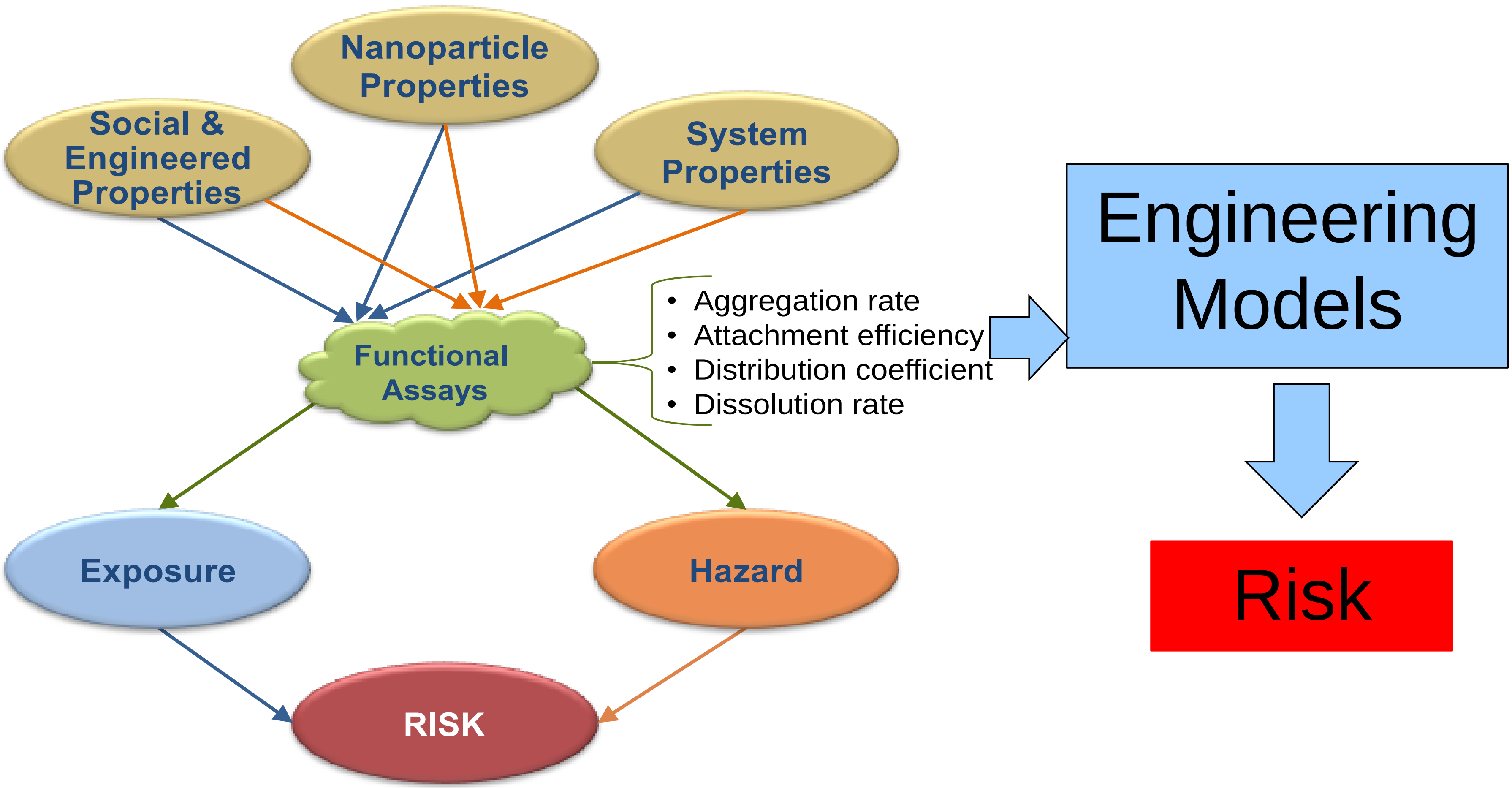
"Functional Assay" Approach to Parameterize Models



This becomes more important as nanomaterial complexity increases

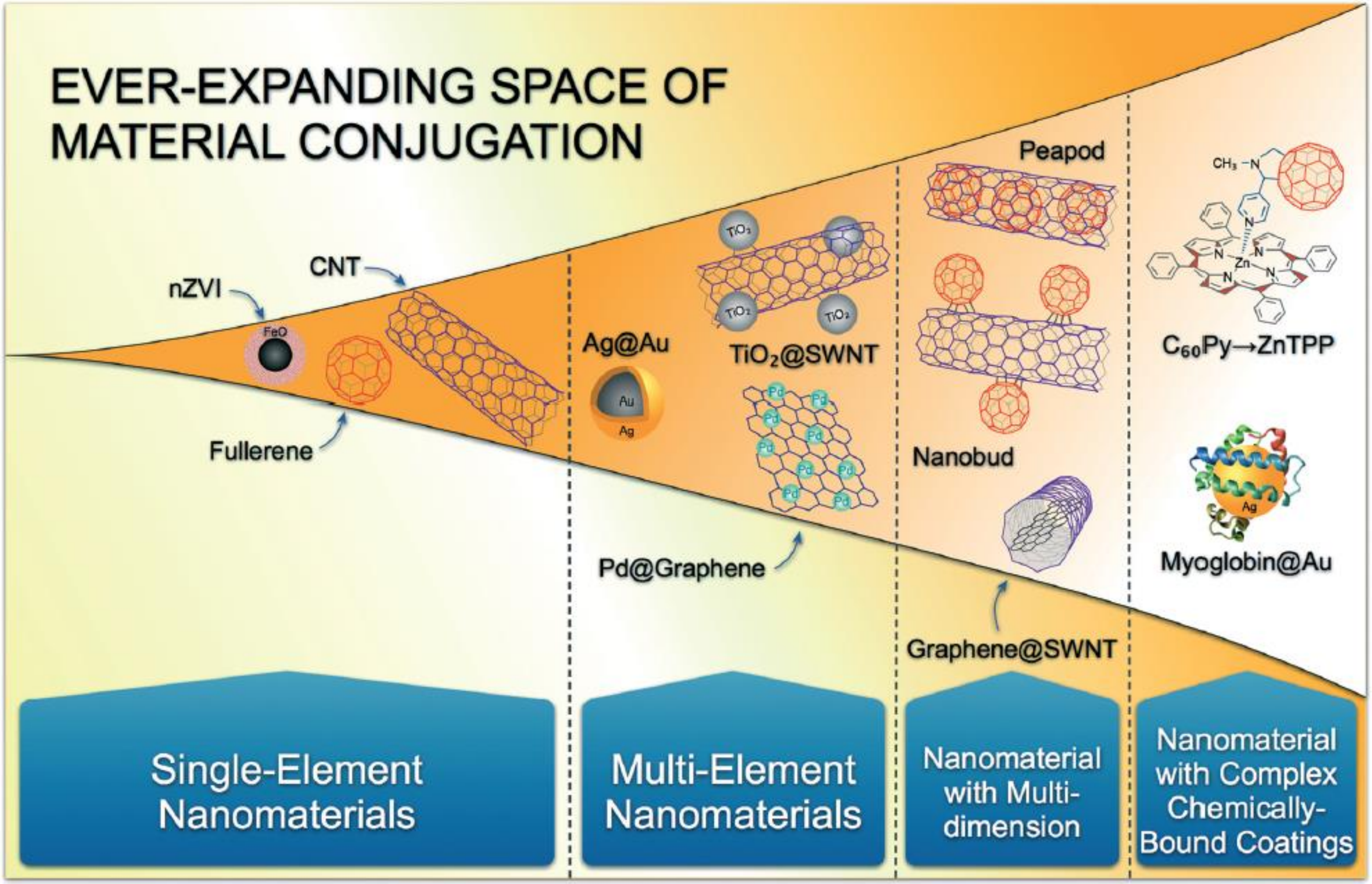


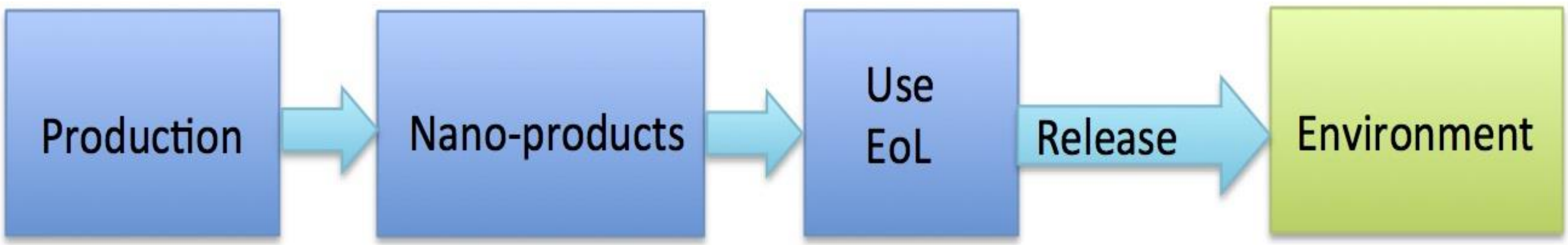
Fig. 3 Schematic showing the ever-expanding space of nanomaterial conjugation and the resulting permutations of nanomaterials.

Saleh et al., 2015 *ES Nano* 2 11-18

Modeling environmental exposure

- Material-flow modeling
  - Sources: Production, use
  - Fate in technical systems: wastewater, solid waste, recycling
  - Provides flows to the environment
- Environmental fate modeling
  - Provides predicted environmental concentrations
  - First tier: Simple box models
  - Second tier: Mechanistic models

Information needs for release modeling



- Total amount
- Geographic distribution

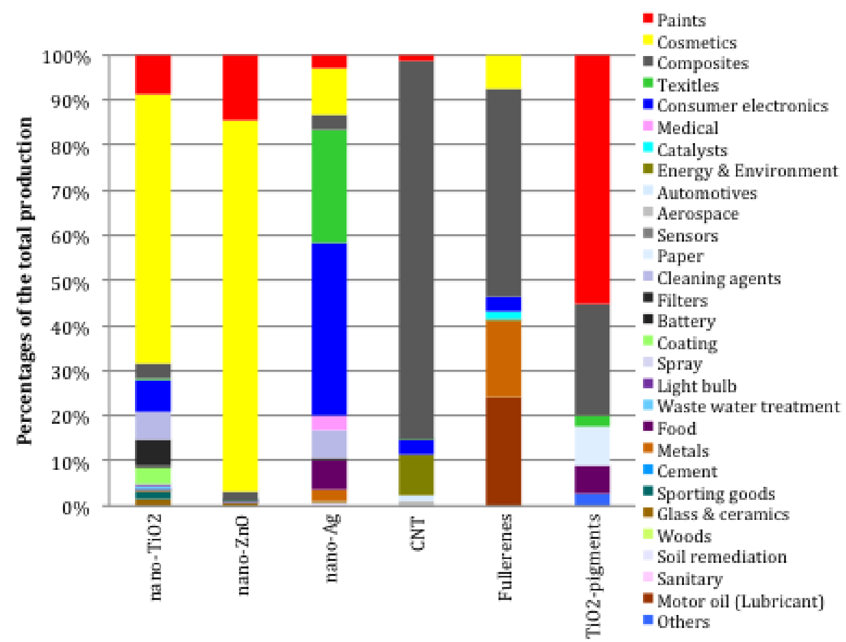
- Relative share of product categories
- Life cycle as determinant

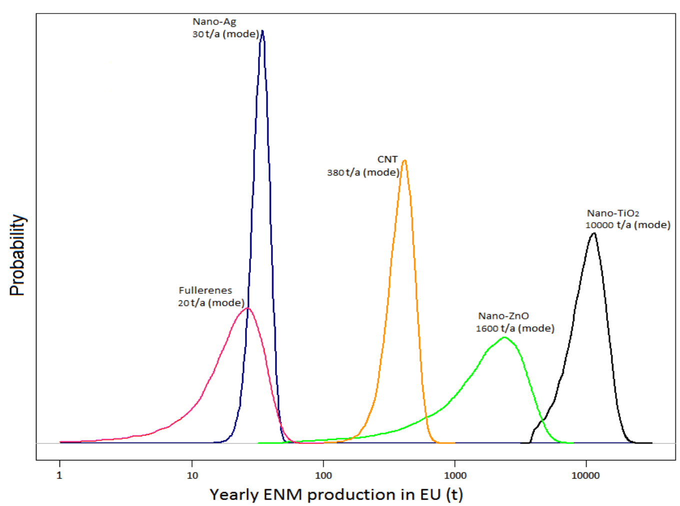
- Potential for release

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

Production and use

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	-	-	-





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

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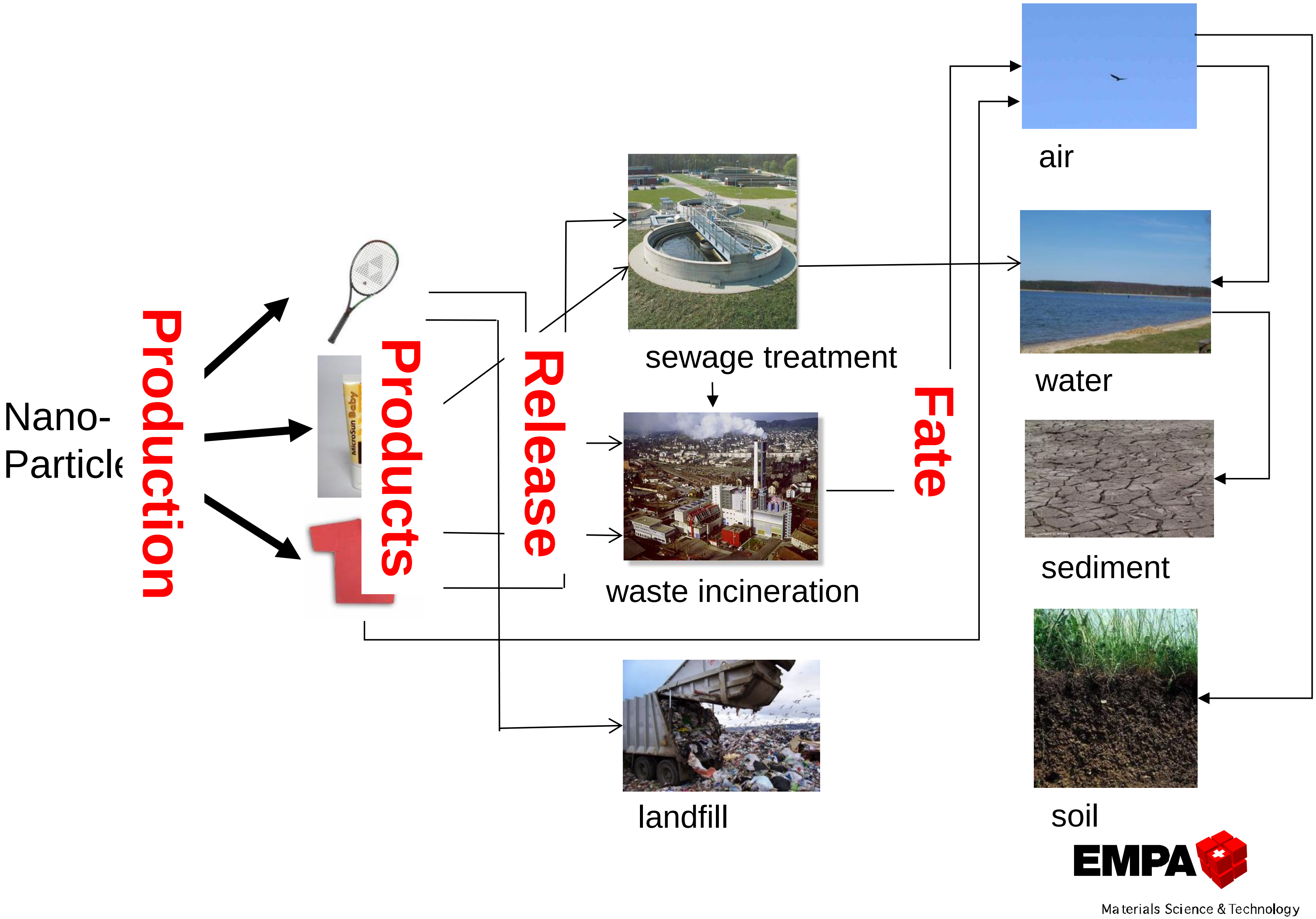
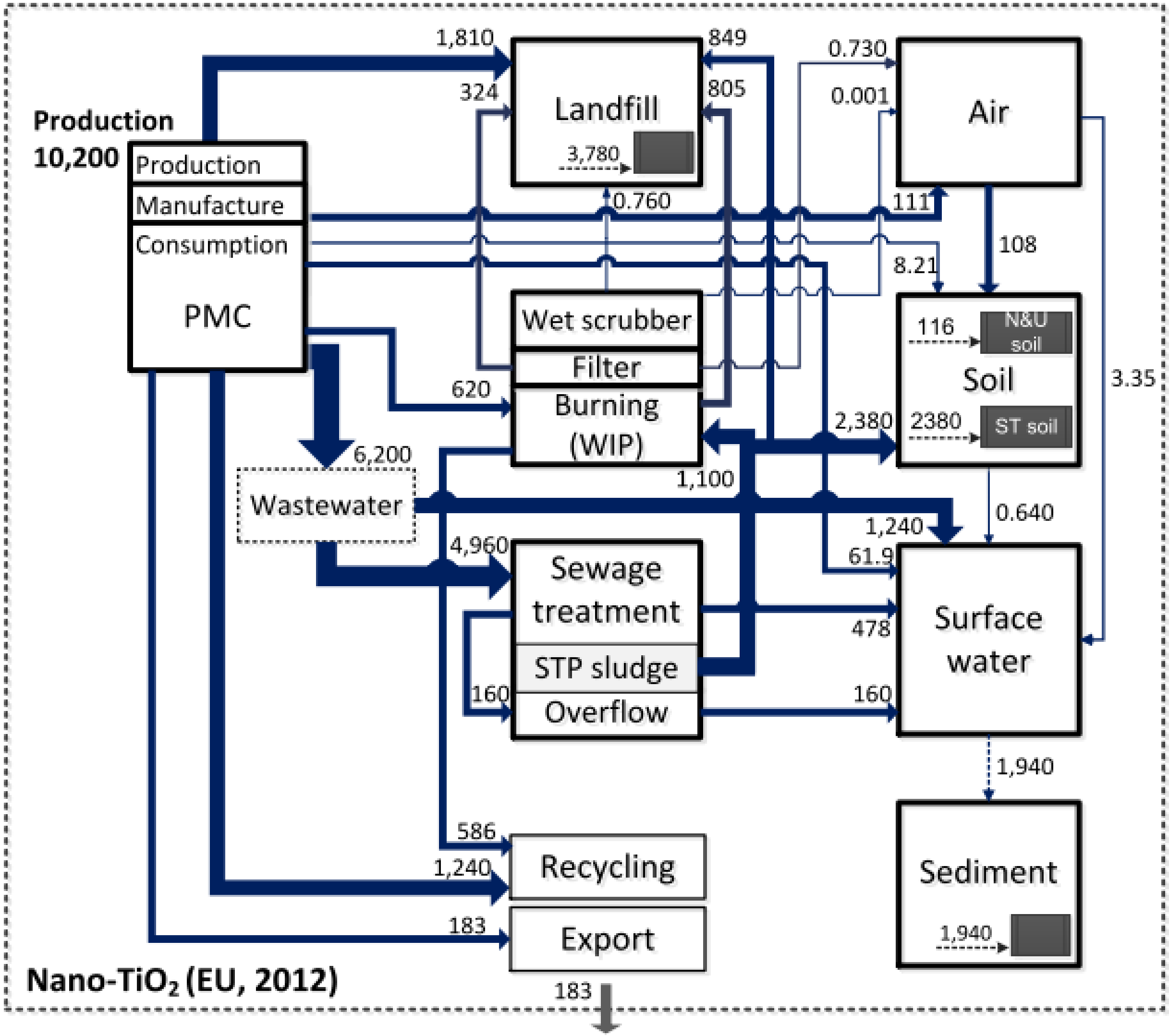
Modeling flows to the environment



Material-flow model for nano-TiO_2 in the EU



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

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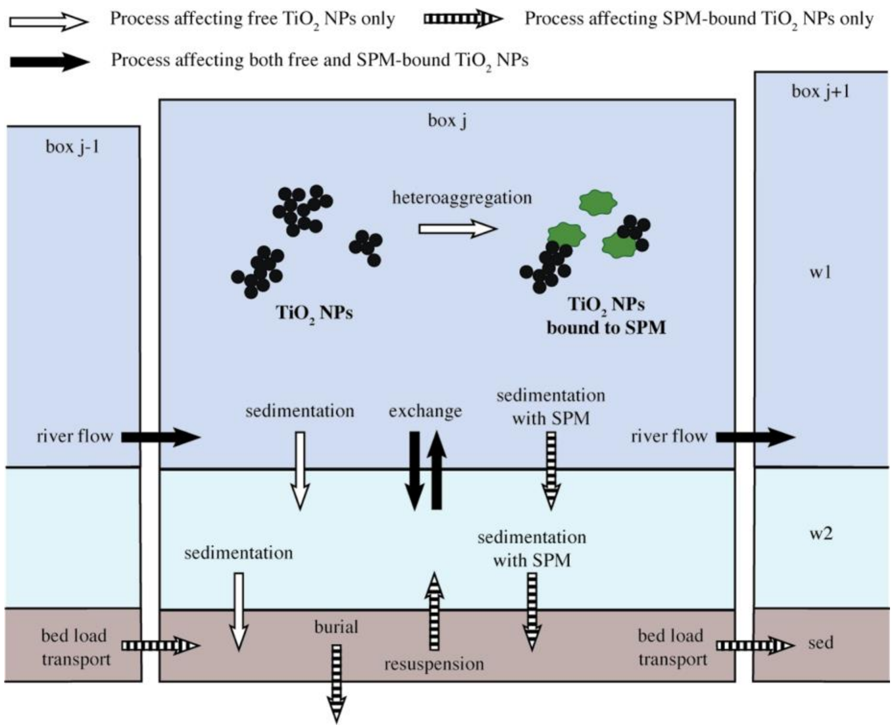
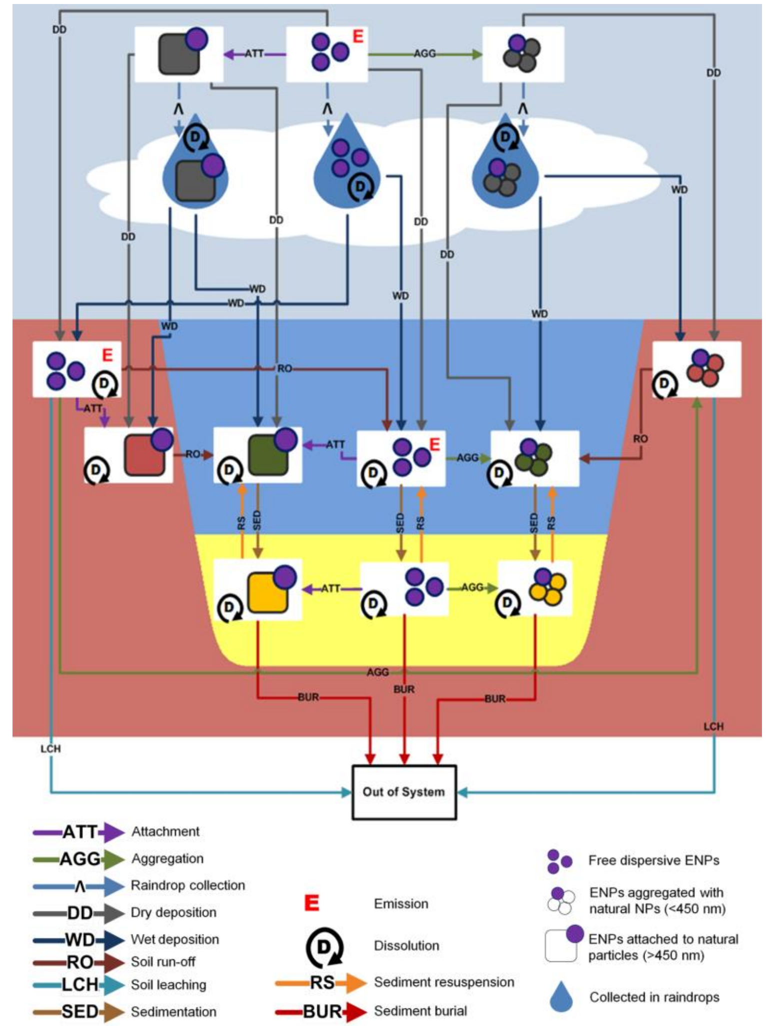
Environmental concentrations

	EU			
	Mode	$Q_{0.15}$	$Q_{0.85}$	
		Nano-TiO_2		
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	µg/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

Fate models for nanomaterials





Praetorius (2012) ES&T 46, 6705

Meesters (2014) ES&T 48, 5726

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Conclusions

- Life-cycle based material flow models are well established
  - Able to provide flows to the environment and estimates of concentrations
  - More production and use data needed
  - Transformations during use and release needs to be included
  - Next level of complexity involves dynamic processes
- First versions of environmental fate models available
  - Rely on flow models for input
  - Average region vs. spatially-resolved
  - Heteroagglomeration as main unknown input
  - Experimental data on heteroagglomeration needed
  - Transformations only marginally covered