
HAZARD ASSESSMENT OF NANOMATERIALS WITH RESPECT TO THE ENVIRONMENT – OVERVIEW AND SELECTED ASPECTS



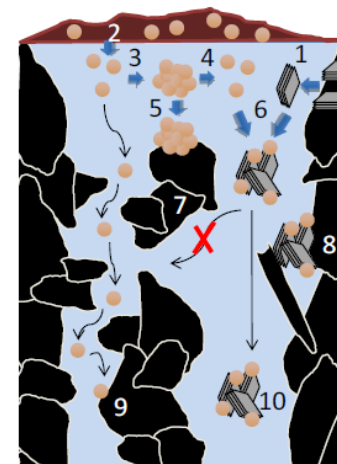
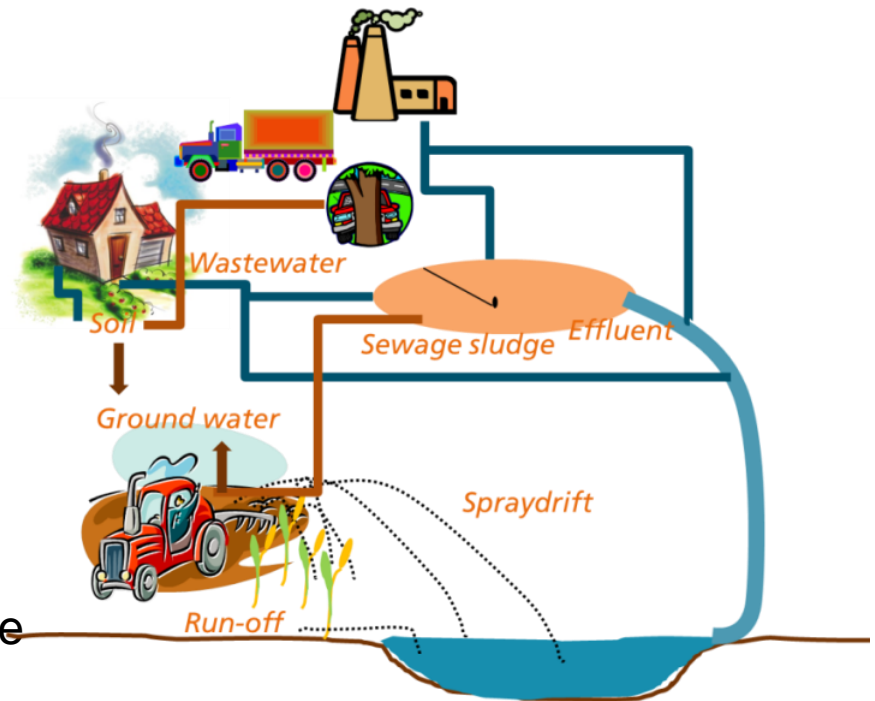
Dr. Kerstin Hund-Rinke

OUTLINE

- Introduction
- Overview on testing
- Selected aspects
 - Test concentrations
 - Illumination
 - Transformation (aging)

Introduction

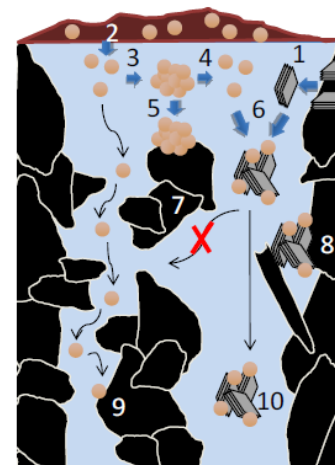
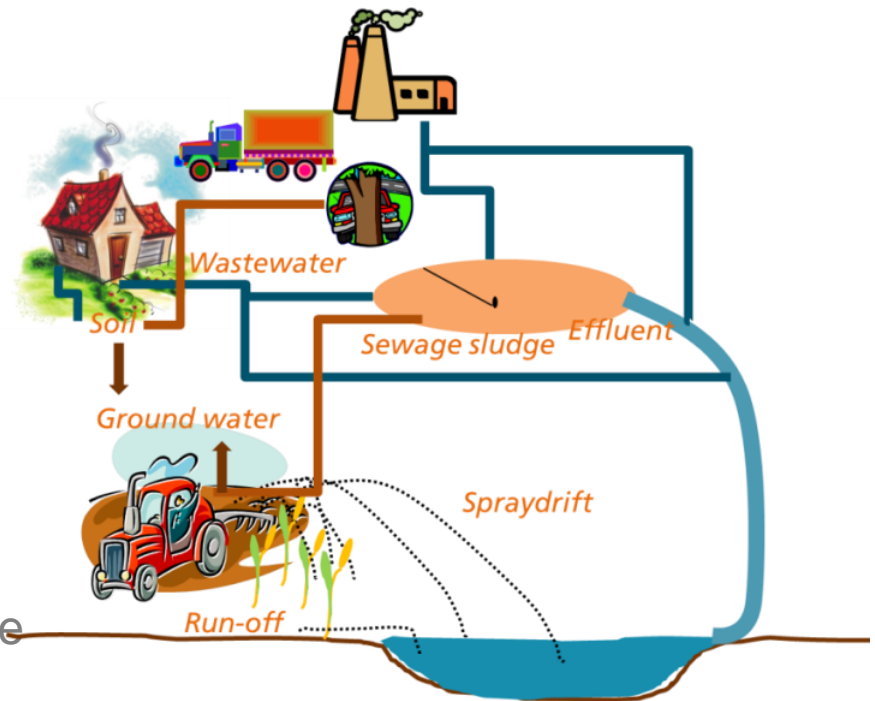
- Regulation in Europe
 - Regulation under REACH
 - Specific area of application (specific legislation)
- Topics under discussion
 - NM to be tested
 - Assessment of NM in any case
 - Exposure driven assessment
 - Life-cycle of NM
 - Release into the environment
 - Durability (loss of NM properties)
 - Environment
 - Primary compartment
 - Secondary compartment



Cornelis et al., 2014

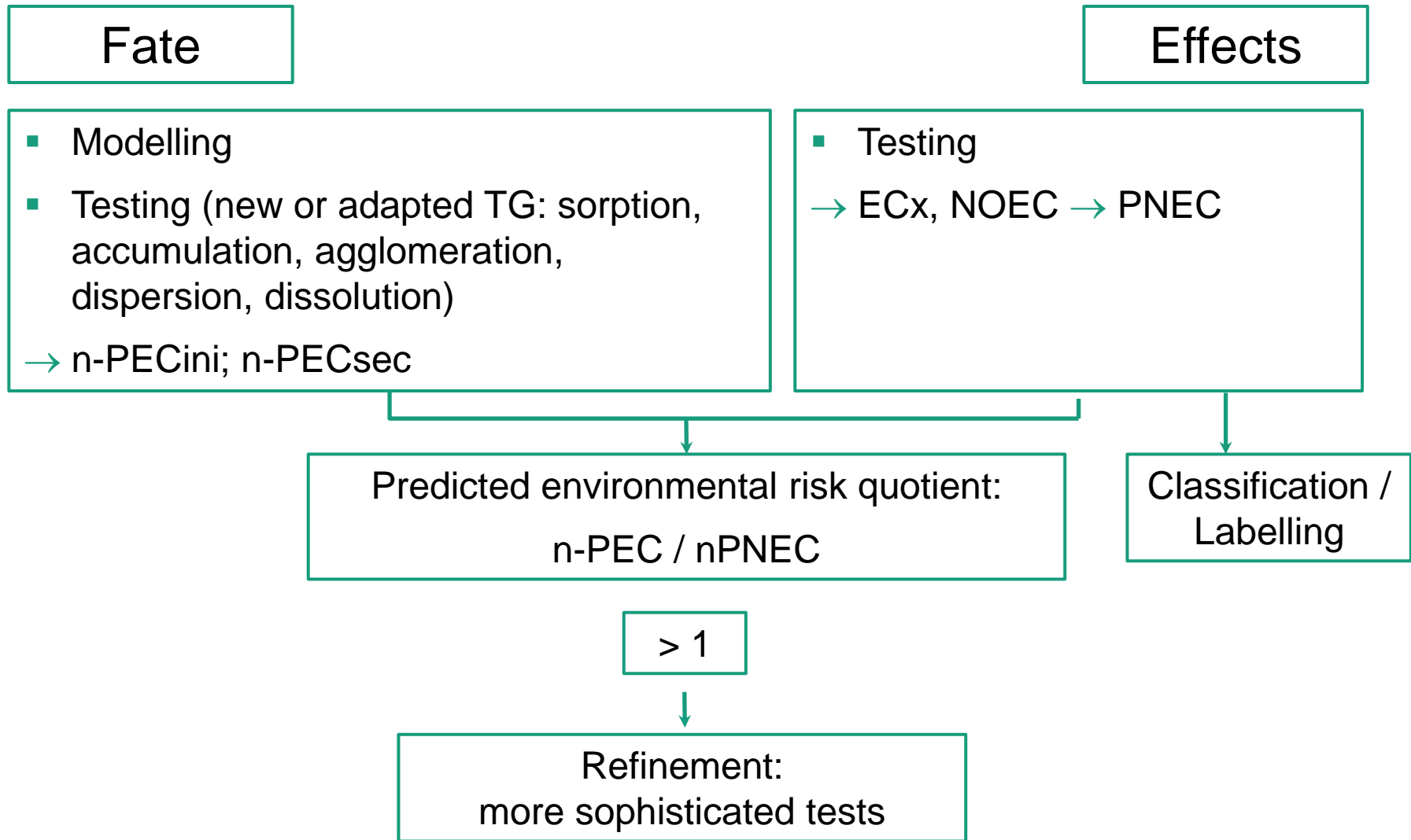
Introduction

- Regulation in Europe
 - Regulation under REACH
 - Specific area of application (specific legislation)
- Topics under discussion
 - NM to be tested
 - Assessment of NM in any case
 - Exposure driven assessment
 - Test strategy
 - Discussion on test methods
 - Discussion on PC-properties suitable as trigger for environmental testing



Cornelis et al., 2014

Assessment of nanomaterials



Test strategy: Tier 1 - Effects

Testing:

Current scope of testing for chemicals: production volume

single species tests: acute aquatic tests → chronic aquatic tests → terrestrial tests

Nanomaterials: exposure differs (sedimentation, agglomeration) → most sensitive compartment still unknown

Proposal: Scope of testing for NM independent of production volume

Aquatic tests *

Sediment tests

Terrestrial tests *

NOEC / EC_x

* Including uptake

Assessment of Hazard

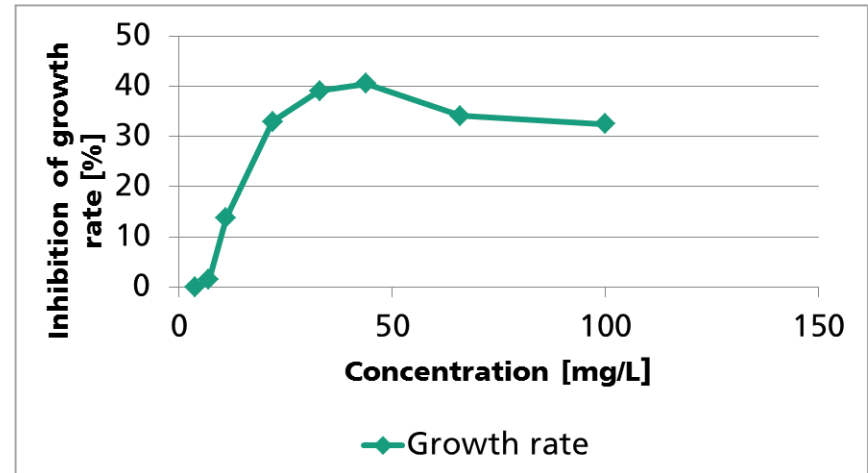
- OECD WPMN (Working Party on Manufactured Nanomaterials)
 - Screening of OECD TGs on ecotoxicity
→ principally suitable
 - Main topics under discussion
 - Application of NM (soil, sediment: dry or wet?)
 - Stability of test dispersion during testing (water: preferably no dispersant / stabilizer / DOM)



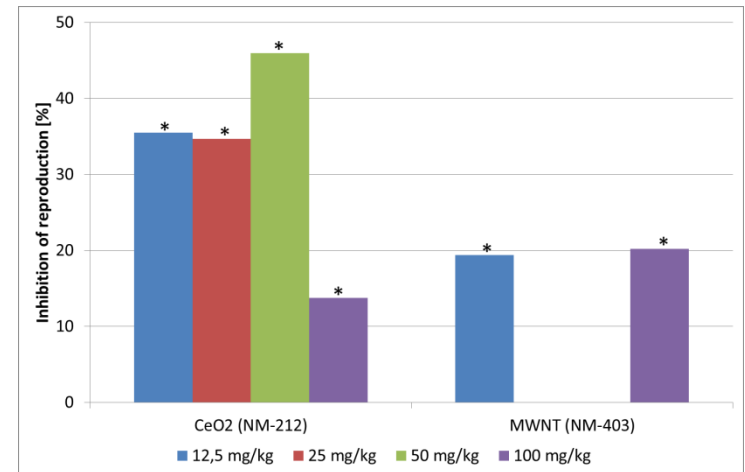
Topic: Test concentrations

- Conventional chemicals
 - Screening: Limit tests
- Nanomaterials
 - Plateau (maximum effect below 100 %) or lower effects in higher test concentrations
→ Several test concentrations
- Recommendation – Testing of NM
No limit test!

TiO₂: growth test with algae

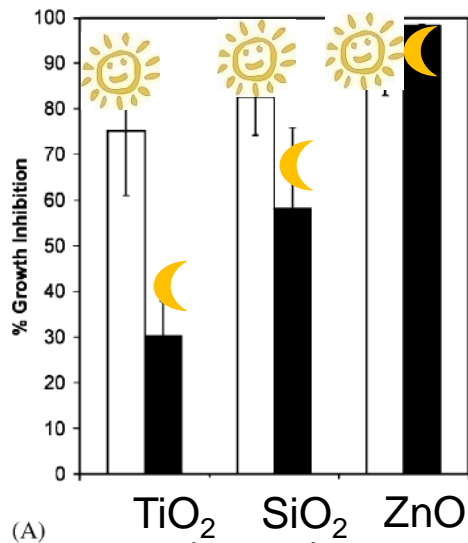


CeO₂, MWCNT: reproduction test with earthworms

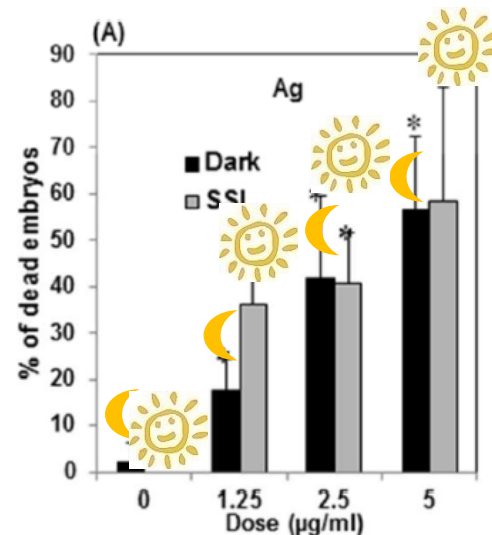


Topic: Illumination

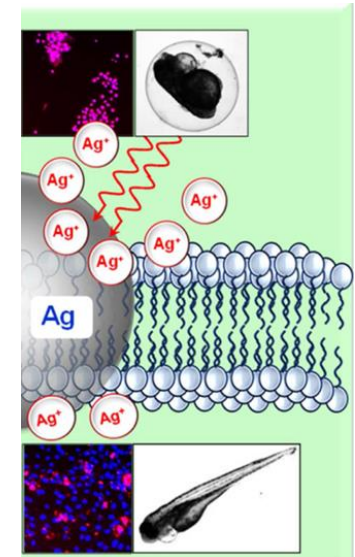
- NM designed for photocatalytic activity (e.g. TiO_2)
 - increased aquatic toxicity if relevant wavelengths are applied
 - no consideration in test guidelines
- Not limited to photocatalytic NM



Adams et al., 2006
 Effect of illumination on growth of *B. subtilis* (■ dark) ☾



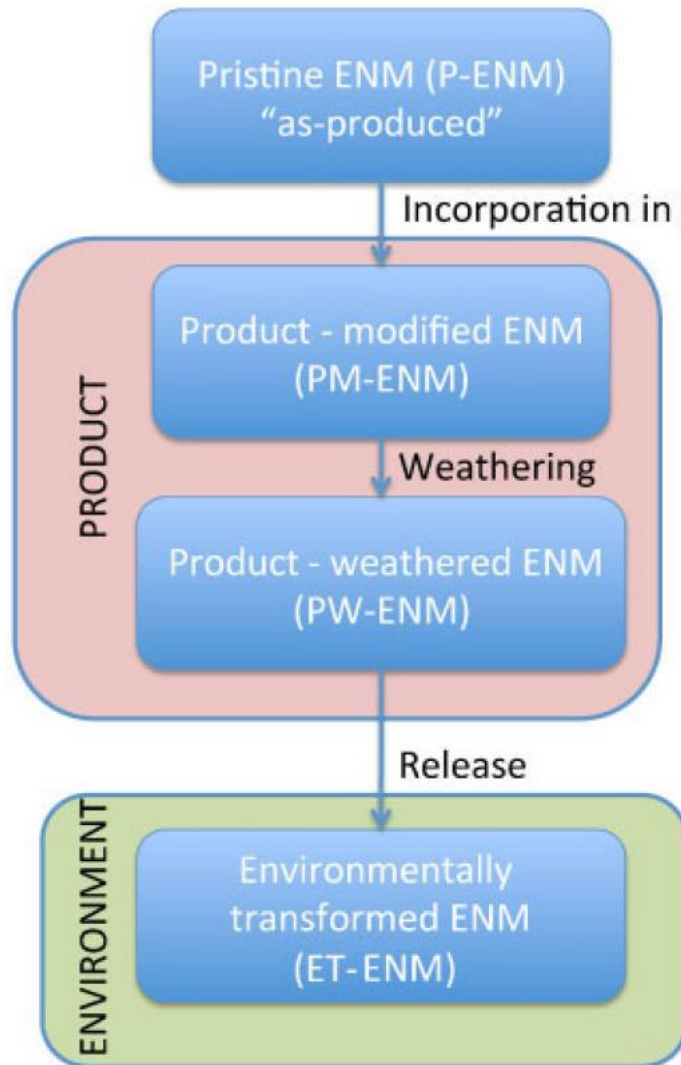
George et al., 2014
 Effect of illumination on fish embryo survival (■ ☾ dark)



Topic: Illumination

- Recommendation
 - Testing applying conventional illumination and lighting with simulated sunlight.
 - Results of test conditions with highest ecotoxicity used for hazard assessment.

Topic: Transformation

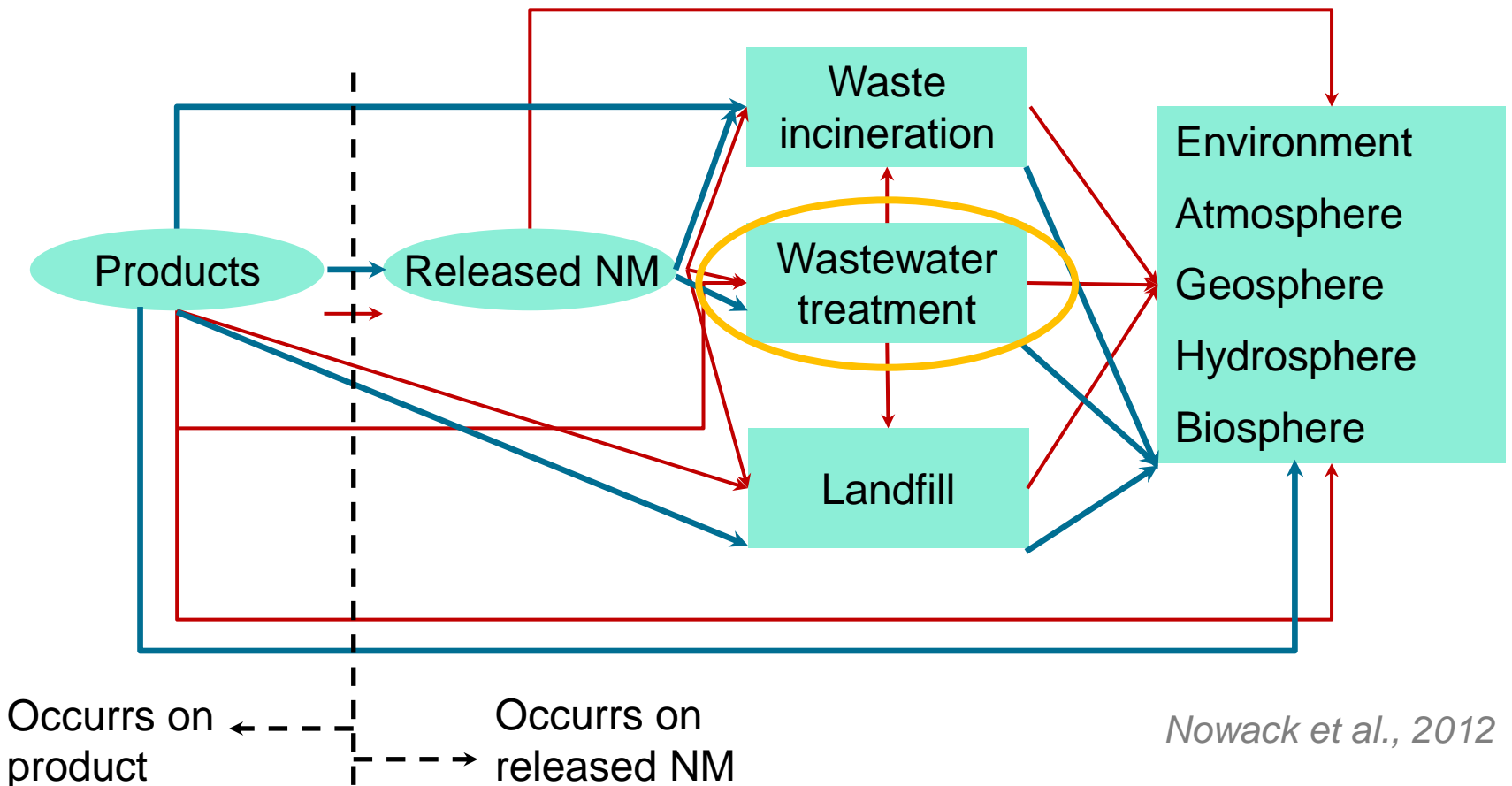


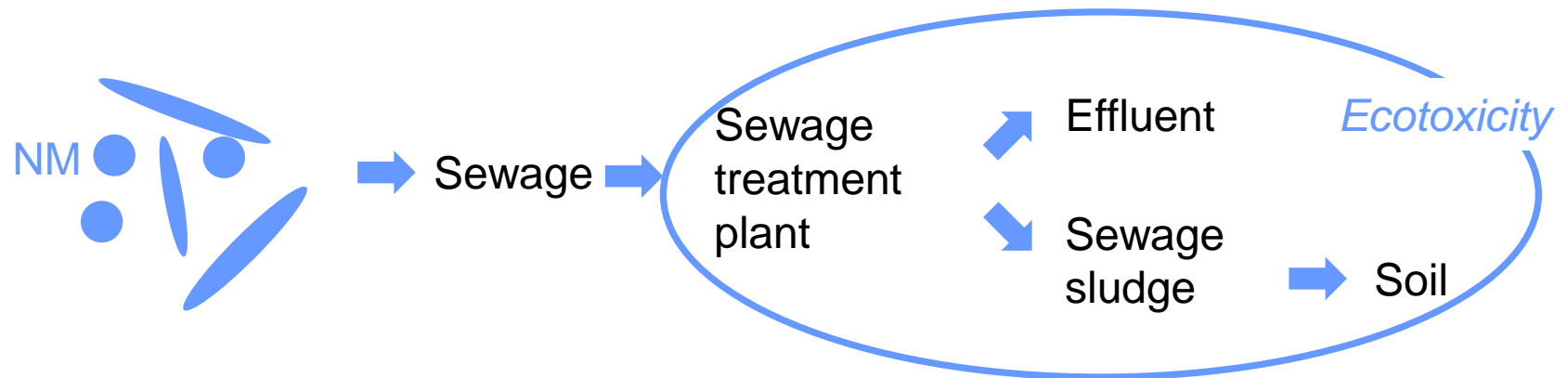
Categorization of engineered nanomaterials

Nowack et al., 2012

Material flow diagram: products → environmental compartments

- Nano-Ag in socks
- Nano-TiO₂ in sunscreen





nano-TiO₂ - Europe:

STP effluent: 0.00347 mg/L

STP sludge: 136 mg/kg

nano-Ag - Europe:

STP effluent: 0.0000425 ng/L

STP sludge: 1.68 mg/kg

Gottschalk et al., 2009

Methods: simulation of sewage treatment plants

■ Model sewage treatment plants

■ OECD 303a

(device designed to determine the elimination and biodegradation of water-soluble organic compounds by aerobic micro-organisms)

■ Denitrification tank, aeration tank ($2 - 3 \text{ mg O}_2/\text{L}$), sedimentation tank

■ Sewage sludge: local wastewater treatment plant

■ Continuous influent (synthetic sewage) and effluent

■ Retention time comparable to industrial-scale plant (6 h); mean sludge time: 10 d

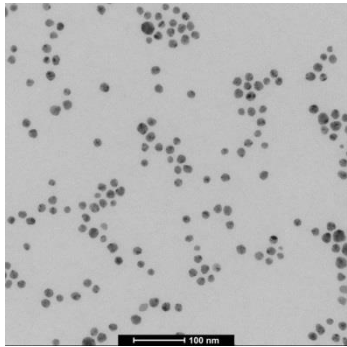
■ Process control

■ DOC , NH_4^+ , NO_2^- , NO_3^-



Methods: Nanomaterial

- Nano silver (OECD Sponsorship Programme)

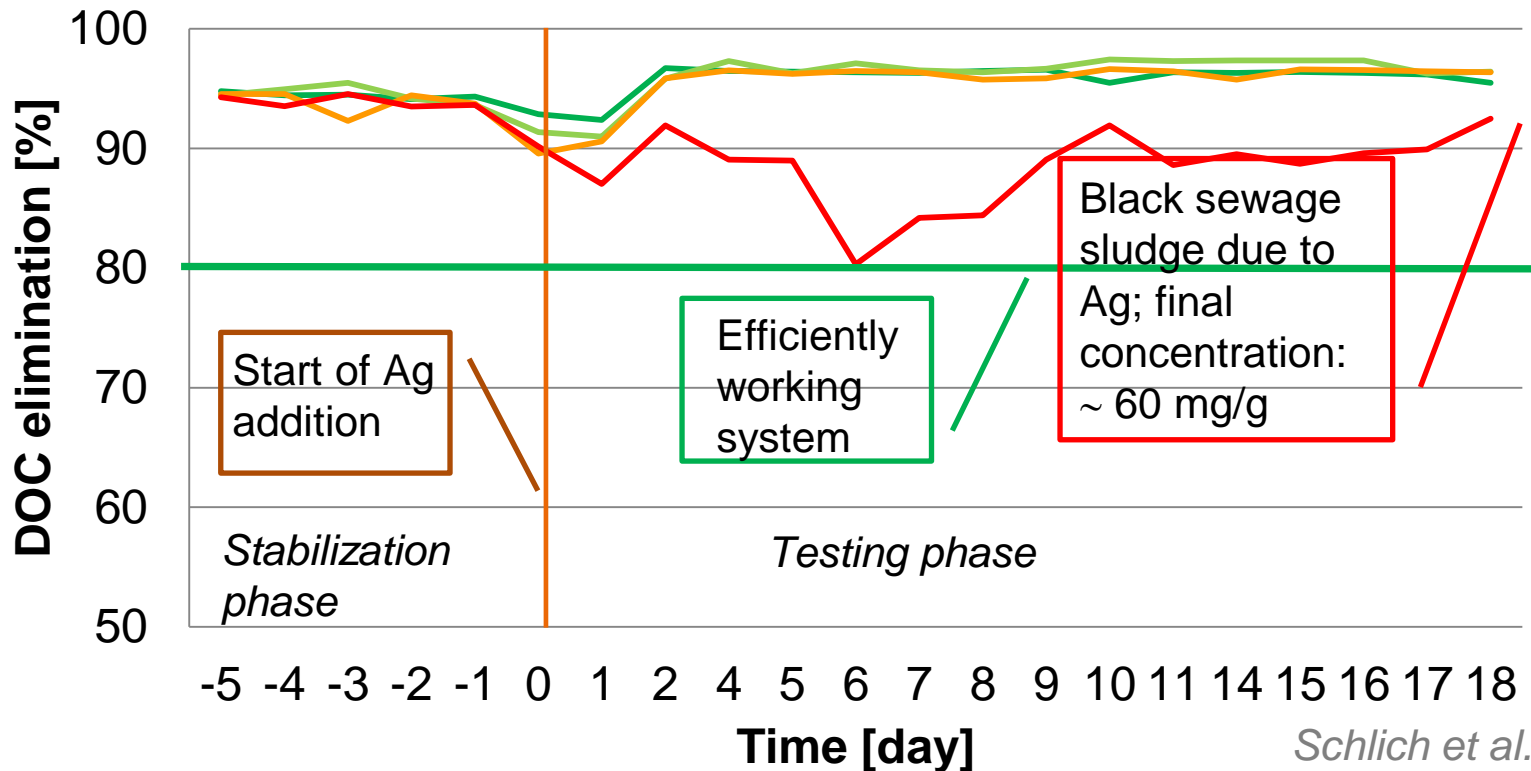


*TEM: Coda Cerva,
Brussels*

- NM-300K
 - Spherical: \varnothing ~15 nm

I. Fate/effect of Ag in sewage treatment plant

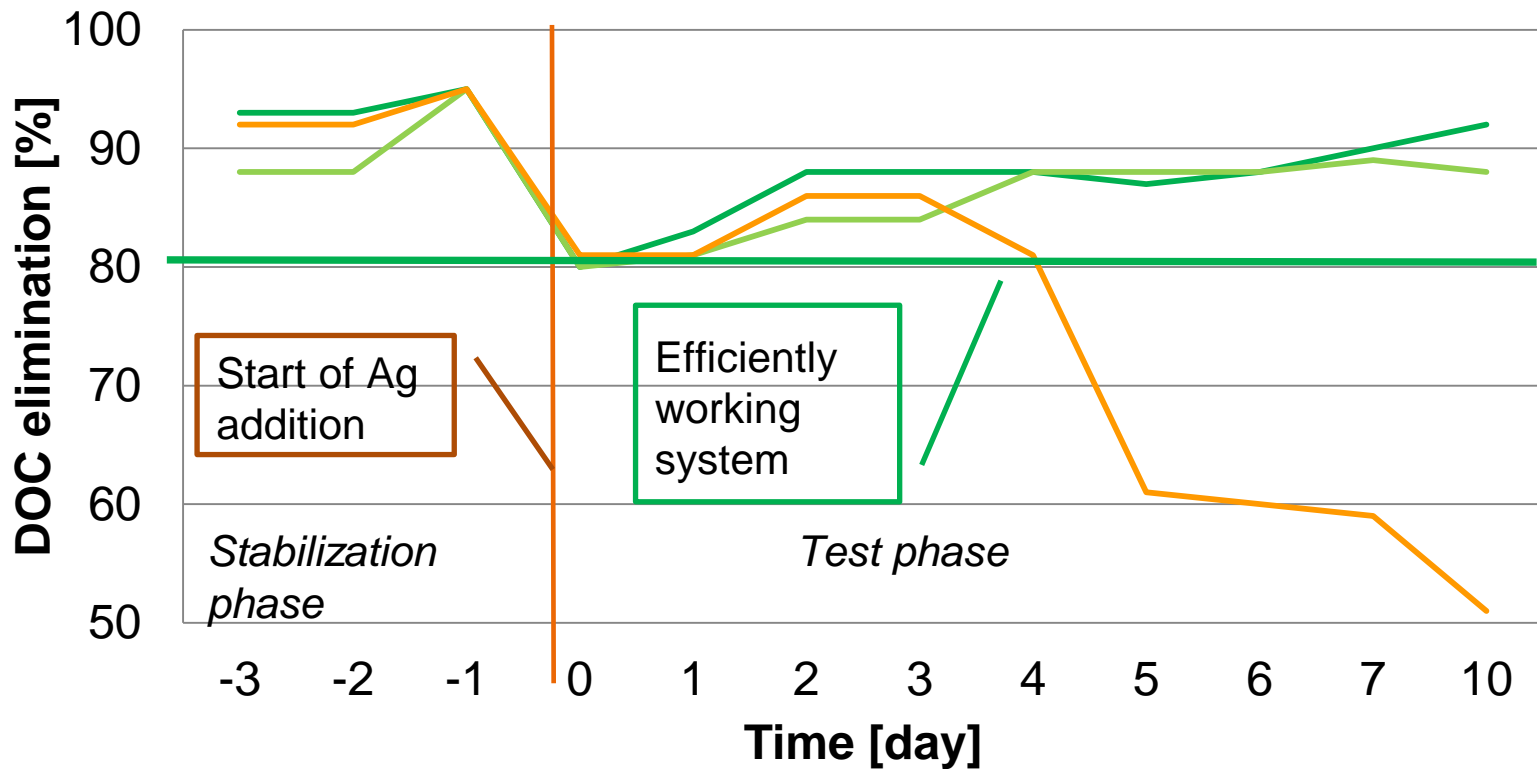
- Continuous influent of nano-Ag: 0.04 – 16 mg/L
- Sorption to sewage sludge; 0.04 – 4 mg/L: ~ 90 %
16 mg/L: 39 – 64 %
- NM-300K : no inhibition of C-degradation



— Control — 1 mg/L — 4 mg/L — 16 mg/L

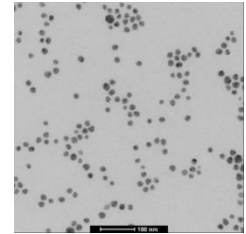
I. Fate/effect of Ag in sewage treatment plants

- Ag (AgNO_3): > 90 % sorption to sewage sludge (0.4 – 2 mg/L)
- Ag (AgNO_3): 4 mg/L: 57 – 99 %
- Inhibition of C-degradation by AgNO_3 (4 mg/L)



Schlich et al., 2013

II. Effluent – NM-300K: Development of fish embryos (OECD 236)

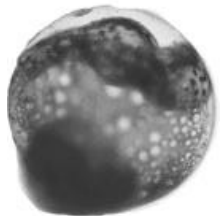


EC50 (48 hpf)

Pristine NM in mineral medium	1.09 mg/L
Pristine NM + control effluent	2.08 mg/L
Effluent	0.14 mg/L



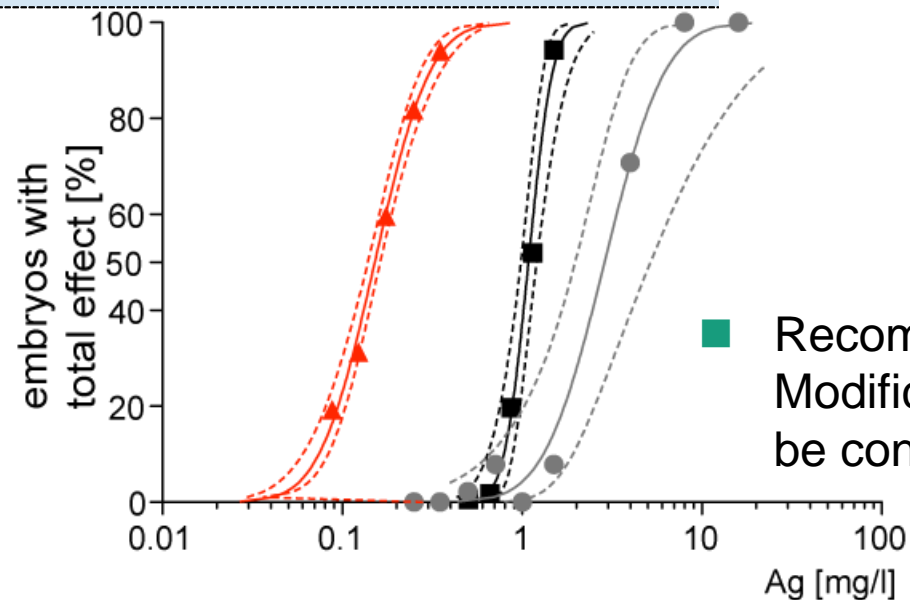
Control



0.87 mg/L



1.5 mg/L



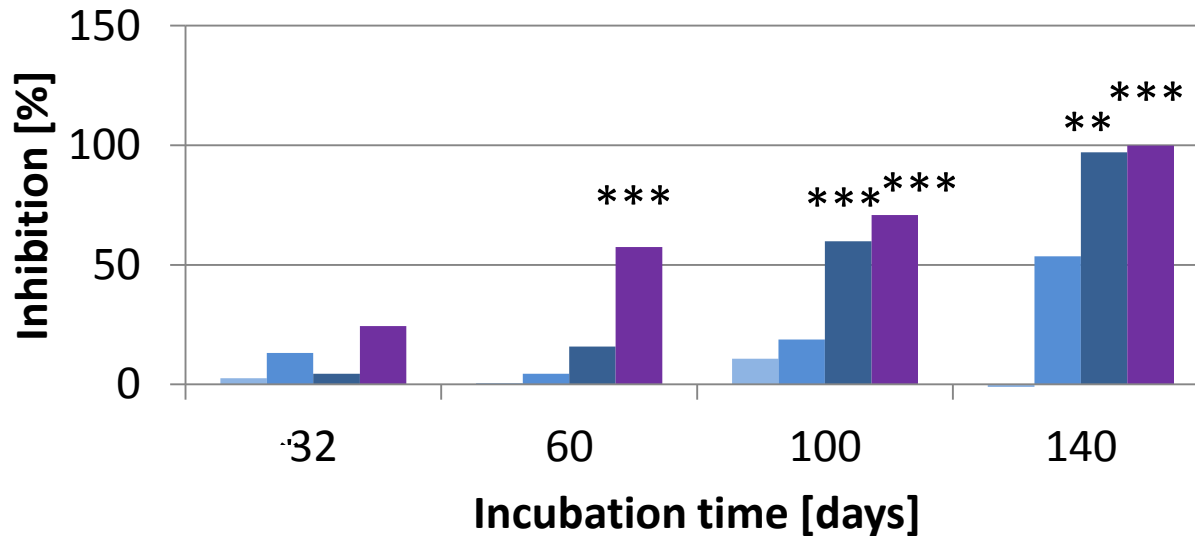
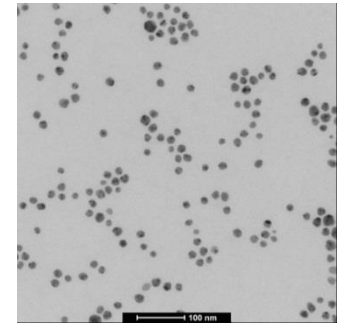
■ Recommendation Modification has to be considered!

- Ag from AgNP in ISO
- Ag from AgNP in effluent (w/o influx)
- ▲ Ag from effluent (influx 16 mg/l AgNP)

Muth-Köhne et al., 2013

III. Soil + sewage sludge – NM-300K: Potential ammonium oxidation (ISO 15685)

	EC50
Pristine NM in soil: 28 d	1.6 mg/kg
Sewage sludge with Ag + soil: 30 d	No effect
Sewage sludge with Ag + soil: 140 d	2.3 mg/kg



■ Bioavailability of NM increases

■ 0.3 mg/kg ■ 2.5 mg/kg ■ 5.2 mg/kg ■ 9 mg/kg

Schlich et al., 2013

Recommendation: Hazard assessment of NM

- Consideration of the three environmental compartments (water, sediment, soil) unless exposure / ecotoxicity can definitely be excluded.
- No limit test, testing of several test concentrations.
- Illumination has to be considered.
- Modification / bioavailability of NM over time has to be considered (aging of NM).

