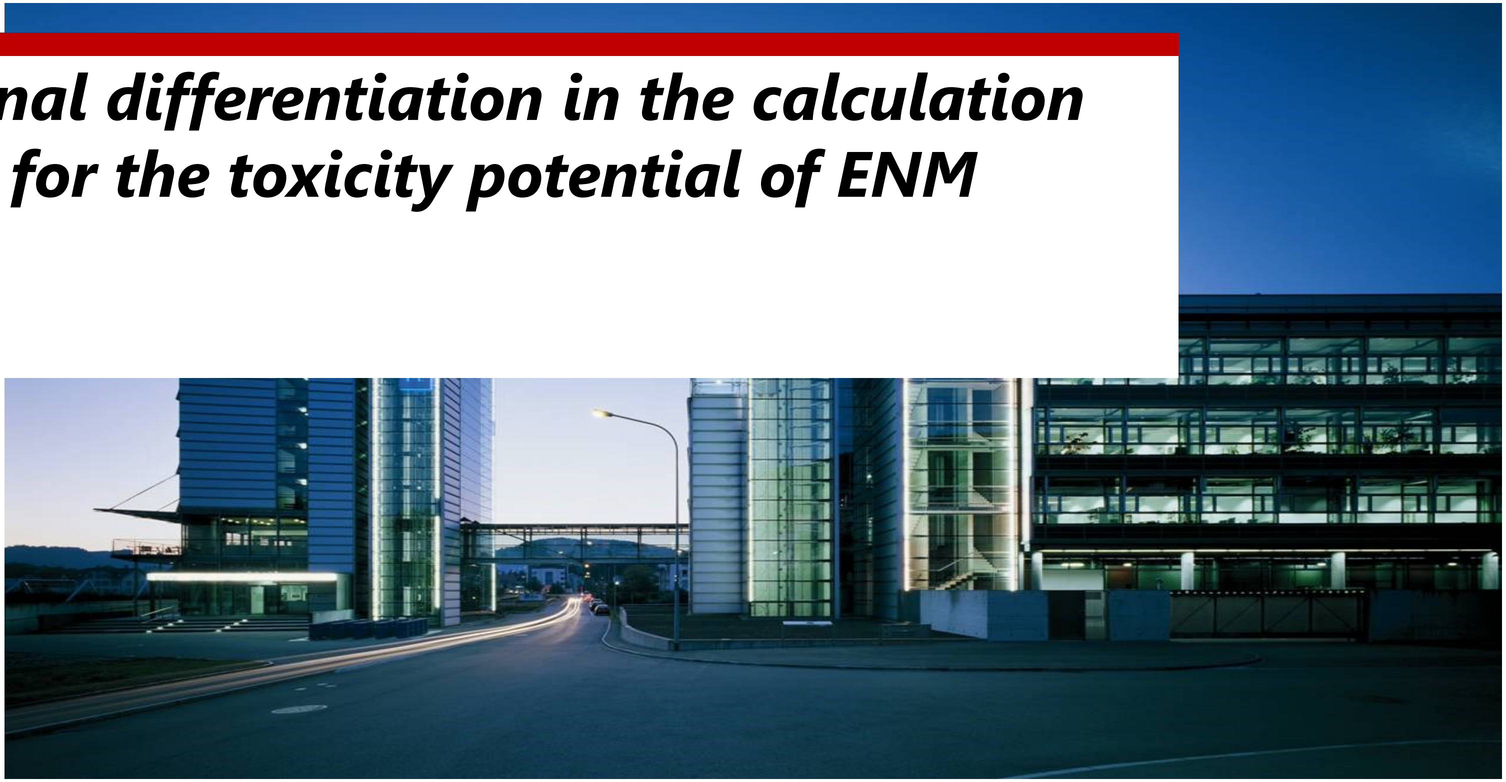
Willkommen
Welcome
Bienvenue

Regional differentiation in the calculation of CF for the toxicity potential of ENM



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INTRODUCTION

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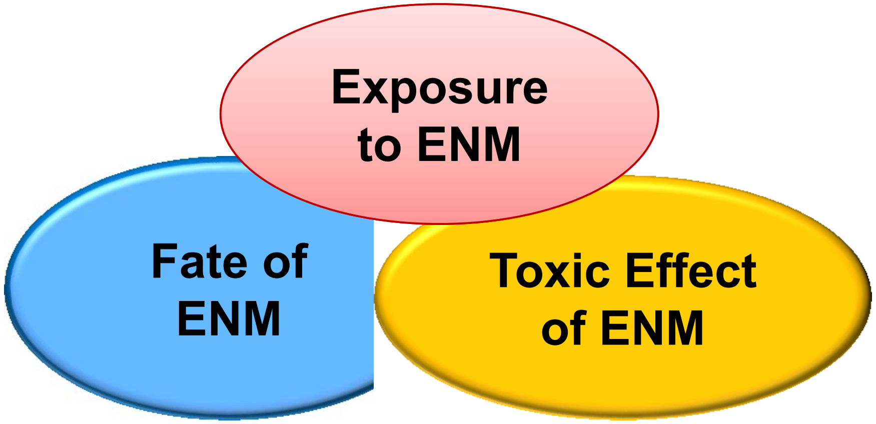
LCA is a tool to assess potential human-environmental impacts of ENM

- LCA studies on ENM are not complete in sense of ISO 14044;
- Lack of assessment of toxic impact category;

Characterisation Factors (CFs) for toxic impact category are still under development



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CF for toxic impact category

- The CF are applied in the step of LCIA to quantify the potential impact;
- Calculated by characterisation method: mostly relied on generic or non-spatial multimedia environmental models;
- Organic substance: environmental fate is described by partition coefficients (e.g. K_{ow});
- Toxic impact: Regional impacts require spatially-differentiated models;

Fate and exposure modeling of ENMs

- Enviromental behaviour is affected by environmental conditions (e.g. ionic strenght, concentration of natural colloid in freshwater);

  Thus, a spatial differentation is required

- Environmental fate models for ENM based on kinetic equations are proposed (Ardvisson 2011, Meester, 2014, Praetorius 2012, Praetorius 2014, Quik 2014);
- Indeed, the partition coefficients seem not be valid for ENM.

USEtox model

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- USEtox is recommended as method for the assessment of toxic impact;
- It provides CFs for organic and inorganic substances for the impact category of Human toxicity and ecotoxicity;

e.g. CF for freshwater ecotoxicity

$$CF = FF \times XF \times EF$$

FATE FACTOR (FF)
Persistence of the substance in the environmental compartment

EXPOSURE FACTOR
Bioavailability of the substance

EFFECT FACTOR
Toxicity of the substance.

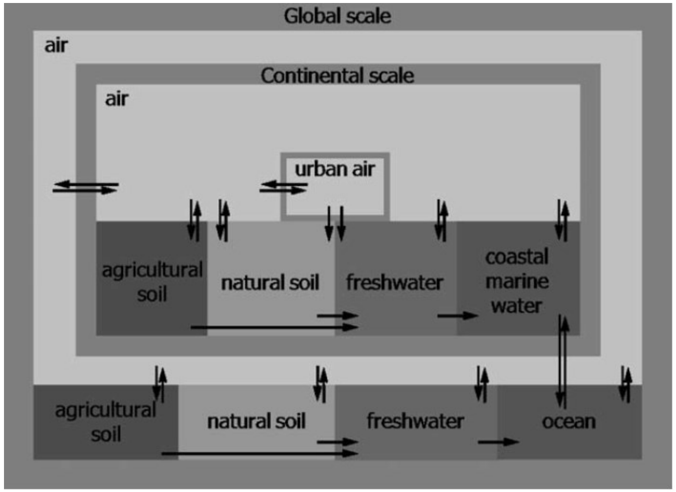
CF for freshwater ecotox.(PAF m^3 day/ kg-emitted) represents the freshwater ecotoxicological impacts of chemicals per mass unit of chemical emitted, where the impact is quantified as the potentially affected fraction (PAF) of species

USEtox model

- USEtox is structured in a matrix framework composed of a series of matrices combining fate with exposure and effect:

$$(CF = \overline{FF} \; x \; \overline{XF} \; x \; \overline{EF}\,)$$

- 2 spatial scales are considered;
- It applies the concept of nested multimedia box model;



Source: Rosenbaum et al., 2008

Fate Factor:

- Environmental process: removal, degradation, advection, transport;
- The environmental processes are quantified in term of rate coefficient (day^{-1});
- Substance data required partition coefficients .

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CF for nano-TiO_2 was calculated:

- USEtox model framework;
- Kinetic equations to descibe the environmental fate;
- Two environmental compartments;
- Continental scale (USEtox default values).

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ELSEVIER

Freshwater ecotoxicity characterisation factor for metal oxide nanoparticles: A case study on titanium dioxide nanoparticle

CrossMark

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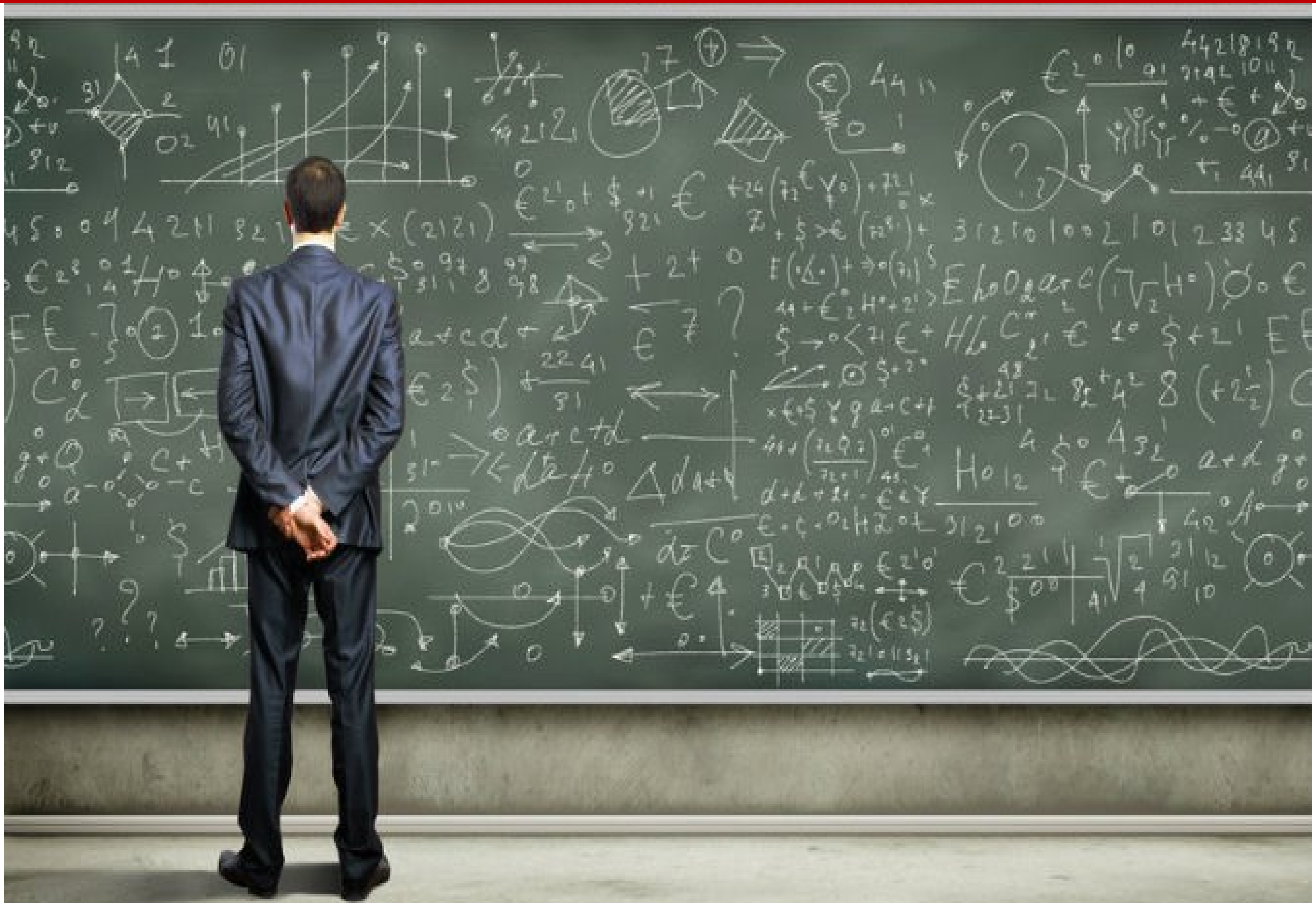
AIM & GOAL

Develop CFs for ENM:

- Fate of ENM is described and calculated by kinetic equation of first order;
- Combining the USEtox model framework and the SimpleBox4nano model;
- Regional variability;

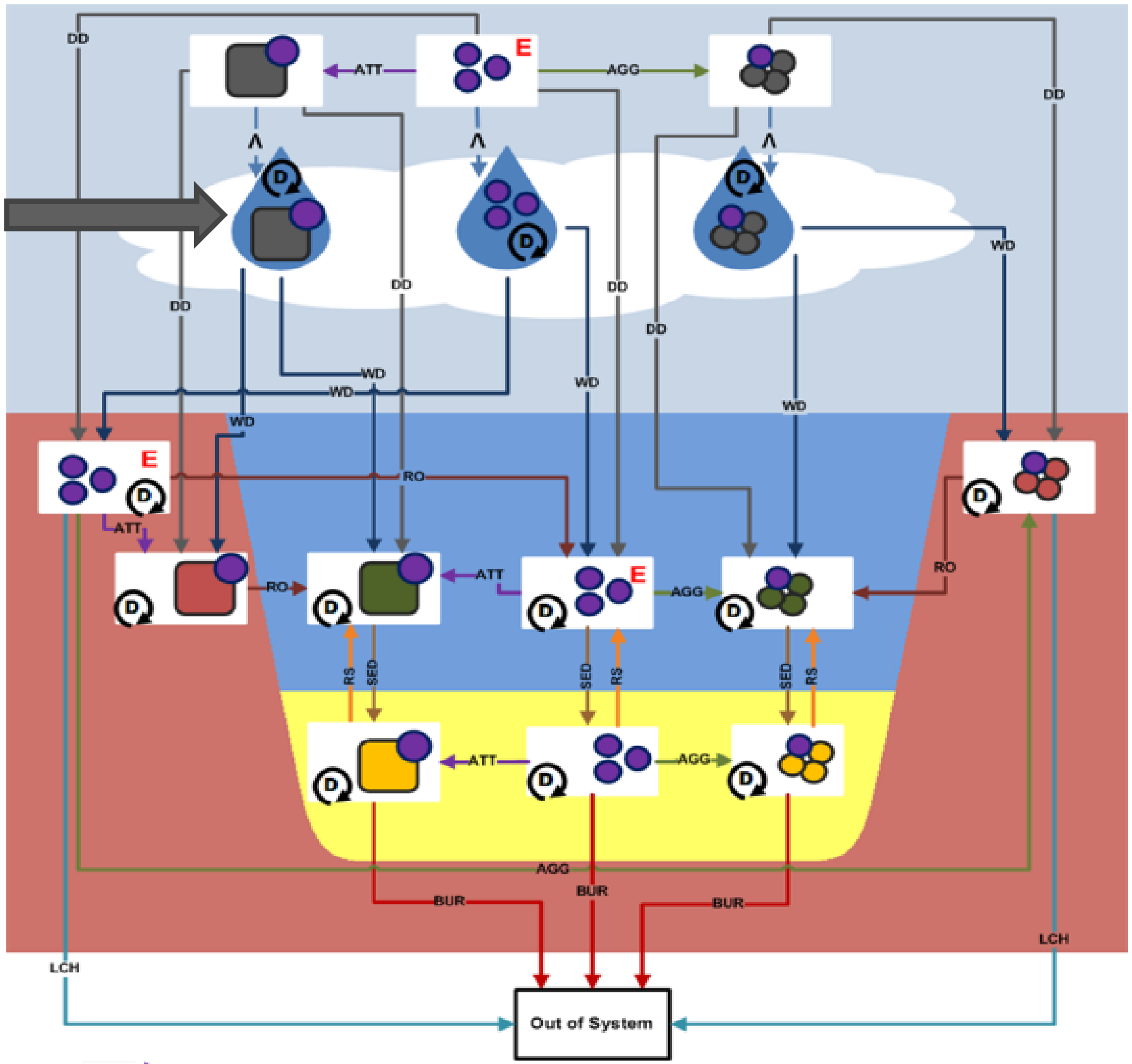
Provide CF based on the state of the art of fate model.

METHOD



1) Environmental processes accounted for by SimpleBox4nano

Wet deposition not included



Source Multimedia modeling of engineered nanoparticles with SimpleBox4nano: model definition and evaluatio . Meester JAJ, Koelmans AA, Quik JTK, et al. Environ.Sci.Technol. 2014, 48, 5726-5736.

2) Environmental processes represented as requested by USEtox

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- Following the USEtox framework the $\overline{FF}$ is calculated as the negative and inverse of the rate coefficient matrix $\overline{k}$;
- Here, the elements of the $\overline{k}$ are the first order rate constant calculated for each one of the environmental processes accounted for;
- The off-diagonal elements ($k_{i,j}$) reflect intermedia or advective transport from compartment *i* to *j* (e.g. air, water, soil);
- The diagonal elements ($k_{i,j}$) represent the negative of the total removal rate coefficient for compartment *i* including biotic/abiotic degradation, advective and intermedia removal.

k matrix	air	freshwater	sediment	soil
air	$k_{air,air}$	$k_{fresh,air}$	$k_{sed,air}$	$k_{soil,sed}$
freshwater	$k_{air,freshw}$	$k_{fresh,fresh}$	$k_{sed,fresh}$	$k_{soil,fresh}$
sediment	[-]	$k_{fresh,sed}$	$k_{sed,sed}$	$k_{soil,sed}$
soil	$k_{air,soil}$	$k_{fresh,soil}$	$k_{sed,soil}$	$k_{soil,soil}$

3) Environmental parameter characterization

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■ Landascape parameter

The environmental media are «box» at three dimensions:

Area-volume-depth/height

At two geographical scales:

Regional scale: Switzerland landascape data;

Continental scale: Europe landascape data;

Source: Meester, 2014;Kounina, 2014;USEtox model

3.1) Environmental parameter characterization

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The medium parameters involved into the calculation of the FF for ENM have been characterised along the two geographical scales

Medium	Environmental Parameter	
Air	Areosol: nucleation, accumulation and coarse mode	Radius, number concentration, density, ect.
Freshwater	Suspended particle matter (SPM), natural colloid (NC)	
Sediment and Soil	Natural colloid in the pore water, soild grain	

E.g. AEROSOL CHARACTERIZATION

Regional: Meteorological stations representative of **regional background condition of Central Europe** (Asmi, 2011)

Continental: Metereological stations in central Europe representative of **CENTRAL EUROPE AEROSOL** (Asmi ,2011; Janeko, 1998)

RESULT

RESULT

k matrix	air	freshwater	sediment	soil
air	$k_{air,air}$	$k_{fresh,air}$	$k_{sed,air}$	$k_{soil,air}$
freshwater	$k_{air,fresh}$	$k_{fresh,fresh}$	$k_{sed,fresh}$	$k_{soil,fresh}$
sediment	[-]	$k_{fresh,sed}$	$k_{sed,sed}$	$k_{soil,sed}$
soil	$k_{air,soil}$	$k_{fresh,soil}$	$k_{sed,soil}$	$k_{soil,soil}$

The k matrix (first order rate constant $-k_{i,j}$, day^{-1}) shows that:

1) As general trend, the elements calculated for the regional scale are one order of magnitude lower than those calculated at the continental scale;

2) Comparing the values with those reported by SimpleBox4nano (Meester, 2014) some differences are also observed.

RESULT

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CF for freshwater ecotoxicity nano-TiO_2

$$CF_w\ (PAF\ day\ m^3\ kg^{-1}) = FF_w \times EF_w \times XF_w$$

- FF Regional= 5.01E-01 (day);
- FF Continental = 8.24E- 02 (day);
- EF = *28.1 (PAF m^3 kg^{-1}) Salieri et al., 2015*
- XF= 1 [-]

	REGIONAL SCALE	CONTINENTAL SCALE
CF	1.41E+01	2.31E+00

CF: Potentially Affected Fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted

RESULT

The framework has been applied to calculate the CF for carbon based ENM

CFw for Fullerene (C60)-Freshwater ecotoxicity

FF_w Regional= 2.34E-02 (day);
EF_w (CNT) = 200 (PAF $m^3\ kg^{-1}$) Eckelman, 2011;
XF =1;

CF_w= *46.7* (PAF day $m^3\ kg^{-1}$)

CF: Potentially Affected Fraction of species (PAF) integrated over time and volume per unit mass of a chemical emitted

CONCLUSION

The research has allowed to:

- Calculate CFs by :
- Following the USEtox framework;
- Appling the kinetic equations proposed by SimpleBox4nano (Meester, 2014);

Thus, the USEtox model and the SimpleBox4nano have been combined

- A first spatial variability, based on two geographical scales, is proposed;

A regional CF for the impact category of freshwater ecotoxicity is proposed

OUTLOOK

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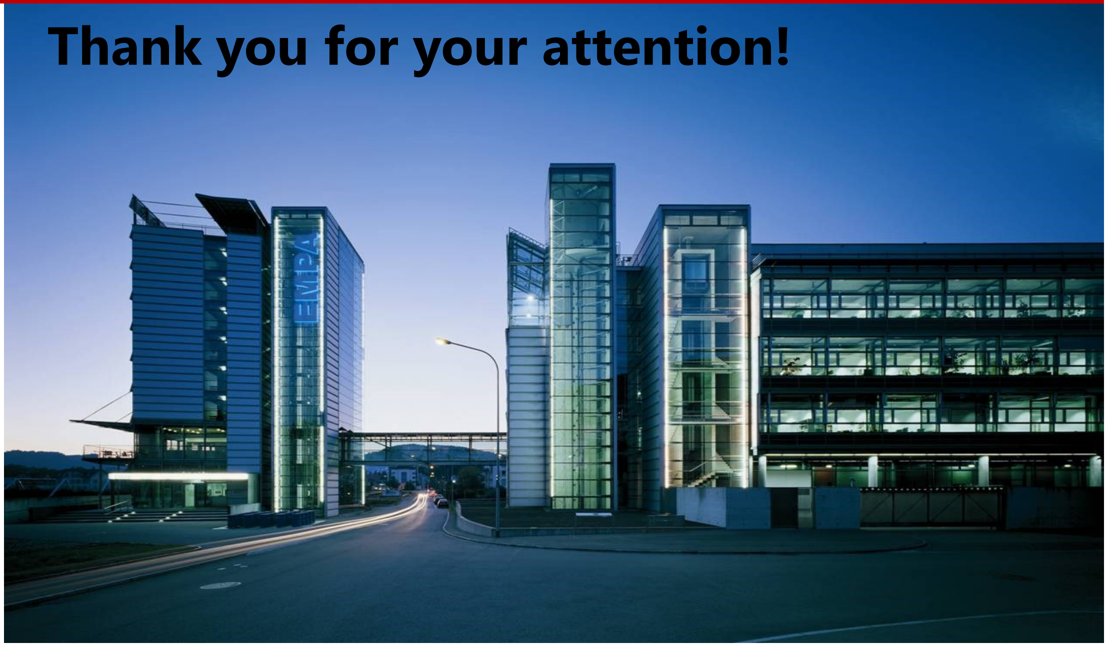
- Sediment and soil compartment:
    - The environmental parameter (e.g. number concentration of NC) have not been regional differentiated;
- Air compartment: include the wet deposition;
- The influence of environmental parameters on the Fate Factor has to be deeper investigated and discussed;
- Further investigation on the exposure factor (XF);
- Expand the Human toxicity CF calculated by Martina Pini (NanoSafe 2014- Grenoble, France);

Thank you for your attention!



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3.1) Environmental parameter characterization-Air

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AEROSOL CHARACTERIZAZION SOURCE:

Regional : Meteorological station it is representative of **regional background condition of Central Europe** (Asmi, 2011)

Continental: Average value of the samples measured at different stations in central Europe that are considered to be representative of **CENTRAL EUROPE AEROSOL** (Asmi ,2011)

Aeresol characterization	Radius (nm)	Density of (kg/m3)	Number concentration (cm^{-3})			Source
			Simple Box 4NANO	Regional	Contiental	
Nucleation mode	25.0	1300	3200	1187	1065	Asmi, 2011
Accumulaton mode	50	1500	2900	2681	3154	Asmi,2011
Coarse mode	1000	1600	0.3	63.5	0.3	Asmi, 2011; Jaeniko 1998

3.1) Environmental parameter characterization-Air

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AEROSOL CHARACTERIZAZION SOURCE:

Regional : Meteorological station representative of **regional background condition of Central Europe** (Asmi, 2011)

Continental: Metereological stations in central Europe that are considered to be representative of **CENTRAL EUROPE AEROSOL** (Asmi ,2011)

Aeresol characterization	**Radius (nm)**	**Density of (kg/m3)**	**Number concentration (cm^{-3})**			**Source**
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Accumulaton mode	50	1500	2900	2681	3154	Asmi,2011
Coarse mode	1000	1600	0.3	63.5	0.3	Asmi, 2011; Jaeniko 1998

3.2) Environmental parameter characterization-Freshwater

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	Simple Box4nano (Meester, 2014)	Regional	Contiental	Reference Regional	Reference Continental
SPM number concentration ($N\ m^{-3}$)	Quik,2014	3.48E+10	2.85E+10	EMPA-EWAG	Praetorius, 2012. Average data of the nuember cocnetration relative ot the Cmass concentration of 30 mg/l
NC number concentration ($N\ m^{-3}$)	1.00E+11	1.00E+11	7.20E+10	Meester,2014	Quik ,2014
Density SPM kg/m3	Not reported	1780	1780	Pretorius,2014 (average data)	Pretorius ,2014 (average data)
Density NC kg/M3	Not reported	1250	1250	Meester, 2014	Meester, 2014
radius SPM m	Not reported	5.00E-06	2.04E-05	Preatorius, 2012, mode of size distribution	Pretorius ,2014 average data on particle size distribution diameter
radius NC m	Not reported	2.91E-07	2.91E-07	Quik 2014 (Rhine river)	Quik 2014 (Rhine river)

Regional Scale: data extrapolated from samples collected at Aare river (Switzerland);
Conitentel scale: the Rhine river has been used as reference for the European area

3.3) Environmental parameter characterization-Sediment/soil

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	SimpleBox4nano (Meester 2014)	Regional/ Conitnental	Reference still to add
Diameter of NC in soil (nm)	Not reported.	120	
Diameter of NC in sediemnt (nm)	Not reported	100	
NC number concentration ($N\ m^{-3}$) in sediment/soil	1.00E+1	1.00E+11	Quick 2014 NC >200nm;Table 1
Density NC in sediment kg/m3	Not reported	2610	
Density NC in soil kg/m 3	Not reported	2500	
Density solid grain in kg/m3	Not reported	2750	Meester 2014
Diametrer grain colelctor (mm)	0.256	0.256	Meester, 2014
Attachment-efficiency (α) with grain	Theoretically derived	2.81E-04	Fang ,2009
Aggregation-efficiency (α) with NC		0.1	Assumed

Partioning coefficient vs first order rate constant

CNT (Eckelman et al., 2012)

- EF =200 PAF $m^3 kg^{-1}$

Worst scenario:

- XF = 100% bioavailable
- FF= 143 days

CF= 29 000 PAF m^3 day kg^{-1}.

"*Here, aggregation and settling are represented by simple partitioning coefficient, but more detailed kinetic modelling would improve the applicability of the model*" (Eckelman et al.,2012)

Several studies followed a kinetic modelling:
Ardvisosn, 2011;
Praetorius et al., 2012;
Meesters et al., 2014

Partioning coefficient vs first order rate constant

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The environmental behaviour of **organic chemicals** and metals ARE assessed using distribution coefficients

These coefficients are quantitative descriptors of how a substance distributes between certain phases (air/water, water/organic carbon, water/soil);

Distribution coefficients have proven extremely powerful for the assessment and prediction of transport, retardation and accumulation of a wide range of substances

Partioning coefficient vs first order rate constant

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Mackay et al., 2006:
"*Current approaches to modeling transport, fate, and effects of materials in the environment are based on properties such as vapor pressure and solubility. Nanomaterials* ***that have very low solubility and very low vapor pressures*** *can nonetheless be highly mobile by virtue of their ability to form metastable suspensions in water and aerosols in air.* ***This metastability renders these classical transport parameters irrelevant***"

Praetorius et al., 2014:
"*ENPs are present in the environment as thermodynamically unstable suspensions and their behaviour must be represented by kinetically controlled attachment and deposition processes as has been established by colloid science"*

The use of "partition coefficients" instead of attachment efficiencies in environmental fate models for ENPs will very likely lead to erroneous results. The entirely kinetic nature of the processes that ENPs undergo in the environment and the heterogeneous nature of nanomaterials are in no way represented by equilibrium partition coefficients.