Significance of physicochemical and uptake kinetics in controlling the toxicity of metallic nanomaterials to aquatic organisms

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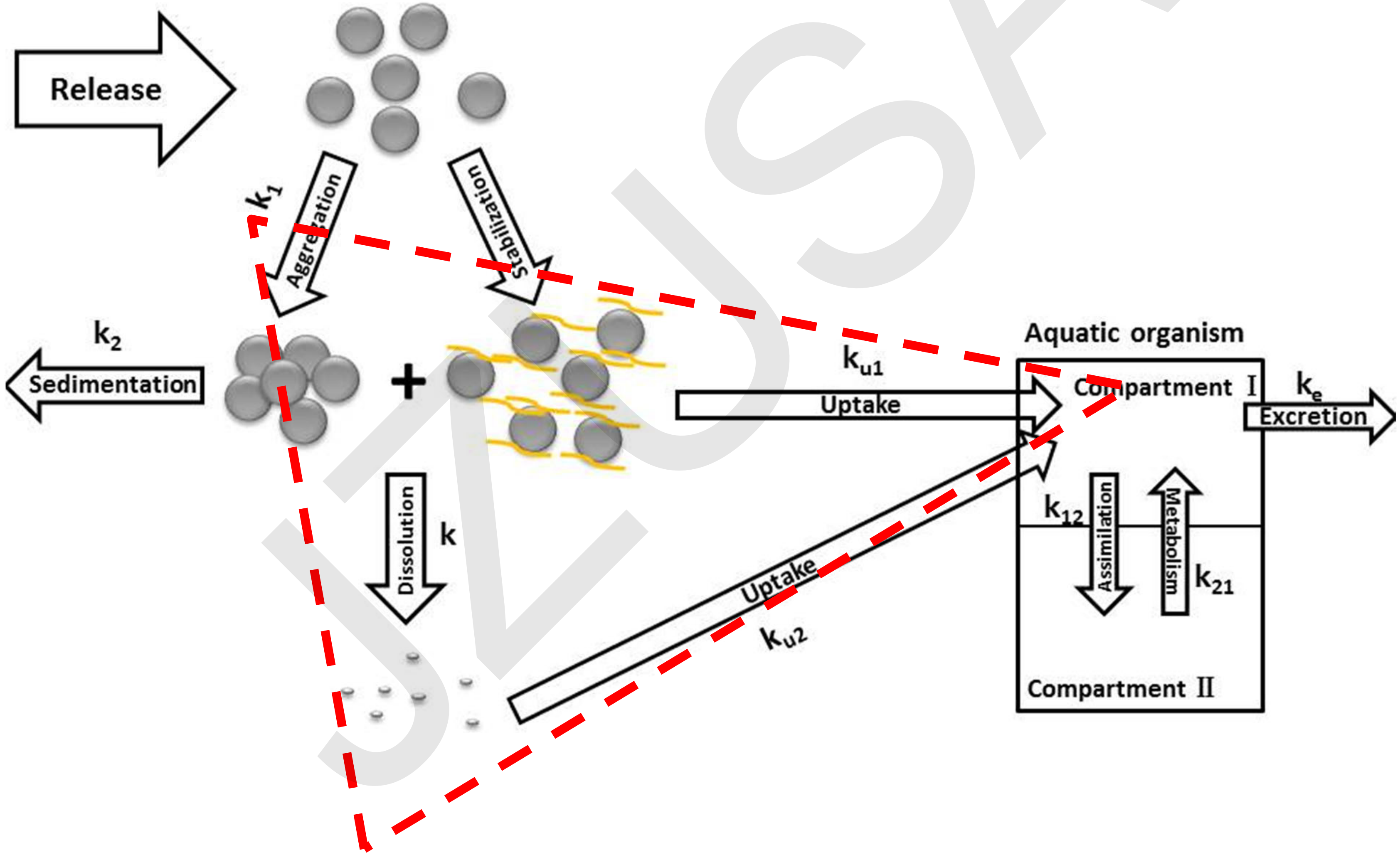
Review scope



Dissolution kinetics and solubility of MNs

Dissolution kinetic models

- **Noyes-Whitney equation:**

$$\frac{dm}{dt} = \frac{DA}{h}(Cs - C)$$

Where dm/dt is the dissolution rate, D is the diffusion coefficient, A is the surface area, and h is the thickness of diffusion layers. Cs is the saturated and C is the bulk concentration.

- **Ostward-Freundlich equation**

$$\frac{S}{So} = \exp[\frac{2\gamma V}{RTr}]$$

Where S is the solubility of fine particles with inscribed radius r, and So is the solubility of the bulk material. V is the molar volume (m^3/mol), γ is the surface energy (J/m^2), R is the gas constant and T is the temperature (K).

Solubility of MNs in nanotoxicological studies

- ZnO-NPs: Solubility: 0.19%~20%, Time for temporal equilibrium: several hours.
- Ag-NPs: Solubility: <8% (most common seen), time for temporal equilibrium: several days.
- TiO_2-NPs: Negligible dissolution.

Biouptake kinetics

- First order - Linear uptake model:

$$I_w = k_u \times C_w$$

This model is assuming the uptake rate (I_w) of metals by the organism is proportional to the metal concentration (C_w) in water, k_u is the uptake rate constant.

- Uptake of nanoparticle:

$$I'_w = k_{u1} \times (C_{NP} + C_{BI}) + k_{u2} \times C_w$$

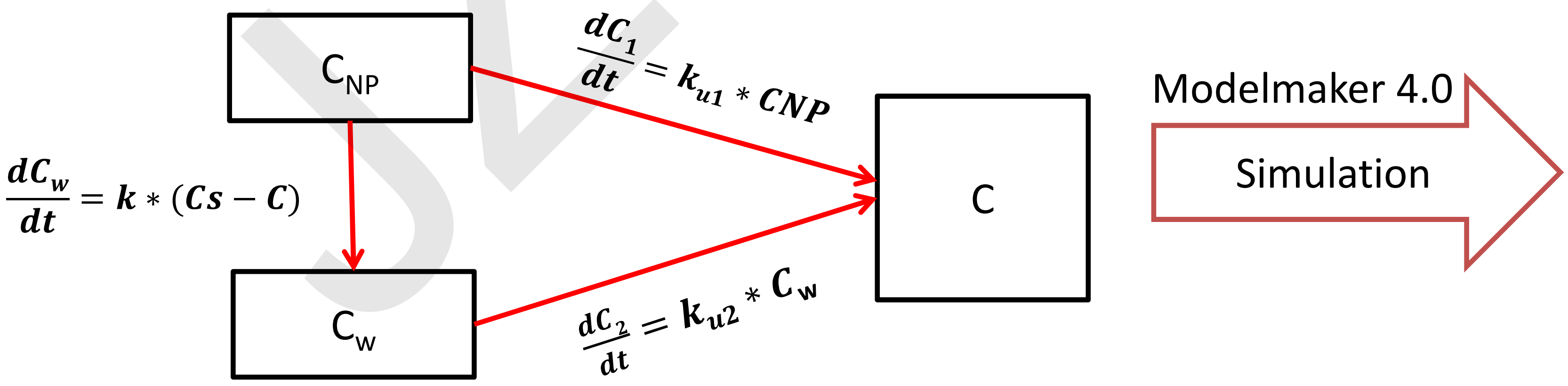
Where k_{u1} is the uptake rate constant of nanoparticles, k_{u2} is the uptake rate constant of dissolved ions, C_{NP} is the concentration of the nanoparticle, C_{BI} is the concentration of nanoparticle bind ion and C_w is the concentration of dissolved ions.

- The total accumulated metal can be written as

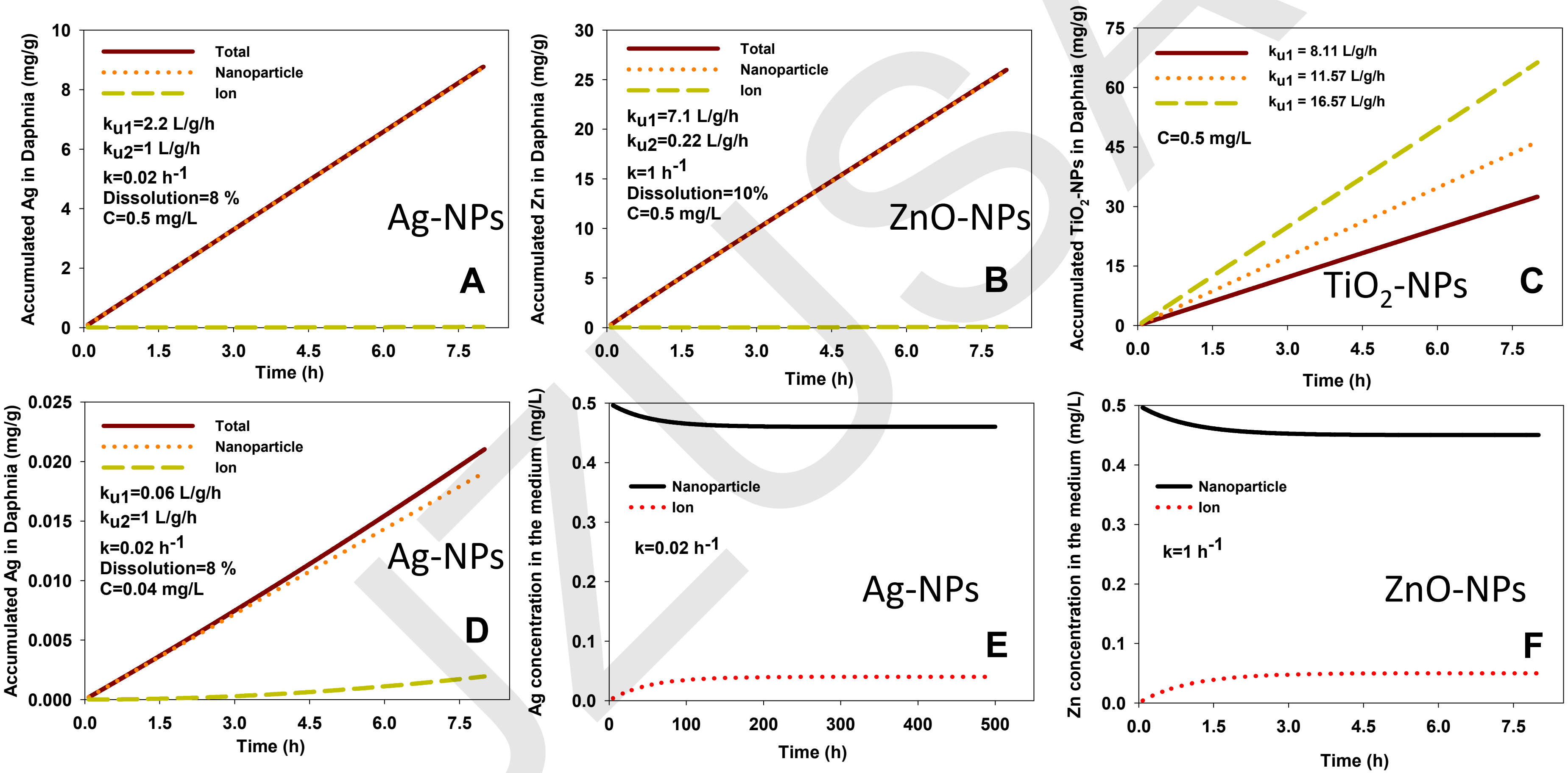
$$C = \int_0^t [k_{u1} \times (C_{NP} + C_{BI}) + k_{u2} \times C_w]\mathrm{d}t$$

Kinetic parameters in Daphnia

Agents	Solubility	k (h^{-1})	k_u (L/g/h)
Zn			0.094-0.359 (2 µg/L)
ZnO-NPs	0.19-20%	0.60-0.138 (20-71 nm)	7.02-7.2 (46-56 nm, 0.5-2 mg/L)
Ag			0.26 (8-880 ng/L) 0.75-1.34 (0.7 µg/L)
Ag-NPs	0.005-38%	0.01-0.55 (4.8-80 nm)	0.25-0.86 (20-100 nm, 1-4 µg/L) **0.06 (40-50 nm, 2-40 µg/L)** **2.2 (40-50 nm, 40-500 µg/L)**
TiO2-NPs	0	0	5.75-23.57 (30-200 nm, 0.1-10 mg/L)



Simulation results



- ✓ Contribution of ion uptake is minor, but still cannot ignore at low nanoparticle concentrations
- ✓ Particle surface properties affect the uptake a lot.

Toxicity and interpretation

Toxicity:

- TiO_2-NPs <<Ag-NPs or ZnO-NPs
- Ion vs Nanoparticle:

Organism	ZnO-NPs	Ag-NPs
Algae	Important	
Zooplankton	Important	Important
Fish	Important	

Interpretation

- Dissolution kinetics:

  ZnO-NPs-Fast; Ag-NPs-Middle; TiO_2-NPs-Hardly

- Bioavailability vs toxicity in Daphnia

Agents	ZnO-NPs	Zinc ions	Ag-NPs	Ag ions	TiO_2-NPs
Bioavailability (k_u)	7.02-7.2	0.094-0.359	0.06-2.2	0.26-1.34	5.75-23.57
Toxicity (LC50)	0.042-4.56	0.76-1.14	0.0018-0.236	0.0008-0.0129	>1.3

✓ Sensitivity: specie specific to certain metal ion
✓ Dissolved ions: growing contribution of ions
✓ Site of action: route of uptake

Main Conclusions

- Different dissolution rates were observed in ZnO-NPs, Ag-NPs and TiO_2-NPs, and their solubilities were also variable in different toxicological studies, leading to a variable and increasing waterborne ion concentration during exposure.
- Varied bioavailability of these MNs and corresponding ions were also found in different aquatic organisms (e.g. algae, zooplankton and fish). Specifically, the MNs appeared to be more bioavailable to daphnids, rendering a minor contribution of ions during short-term exposure.
- Partial toxicity of ZnO-NPs and Ag-NPs was attributed to the dissolved ions, while the toxicity of TiO_2-NPs was mainly due to the generated reactive oxygen species (ROS).
- Overall, this review emphasizes the importance of integrating physicochemical kinetics and uptake kinetics in evaluating the bioavailability and toxicity of both MNs and dissolved ions.