National Academies of Science, Engineering & Medicine

Fate & ecotoxicity considerations for nanomaterials used in sunscreens

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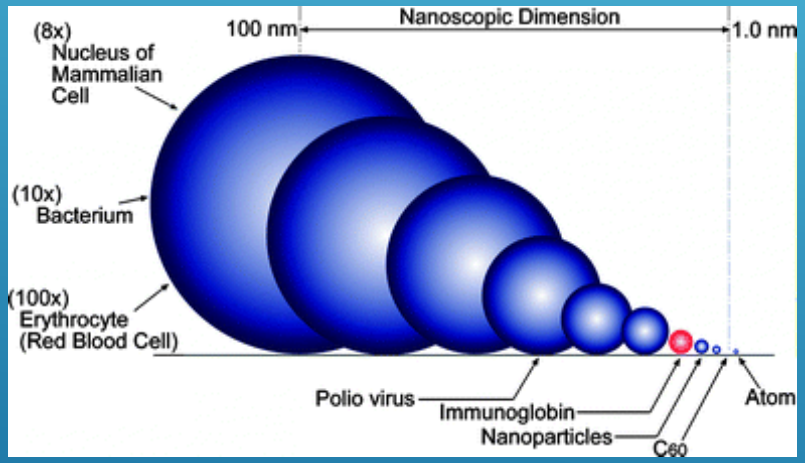
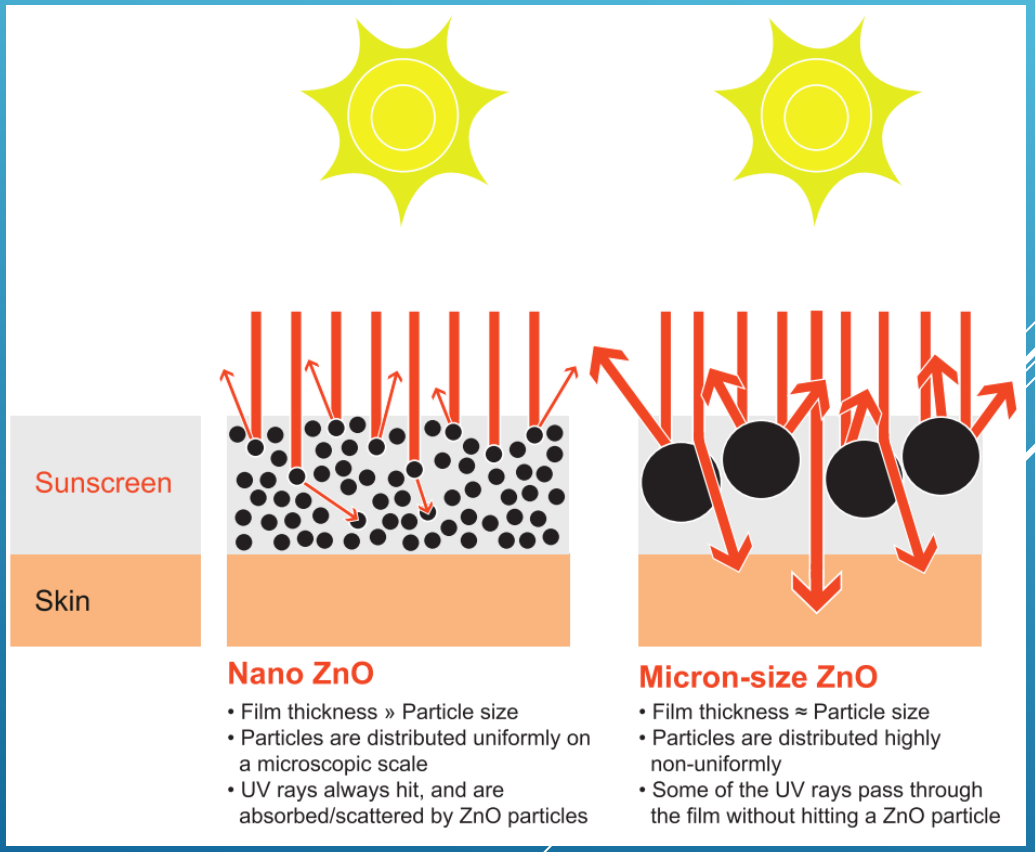
NANO IN SUNSCREEN

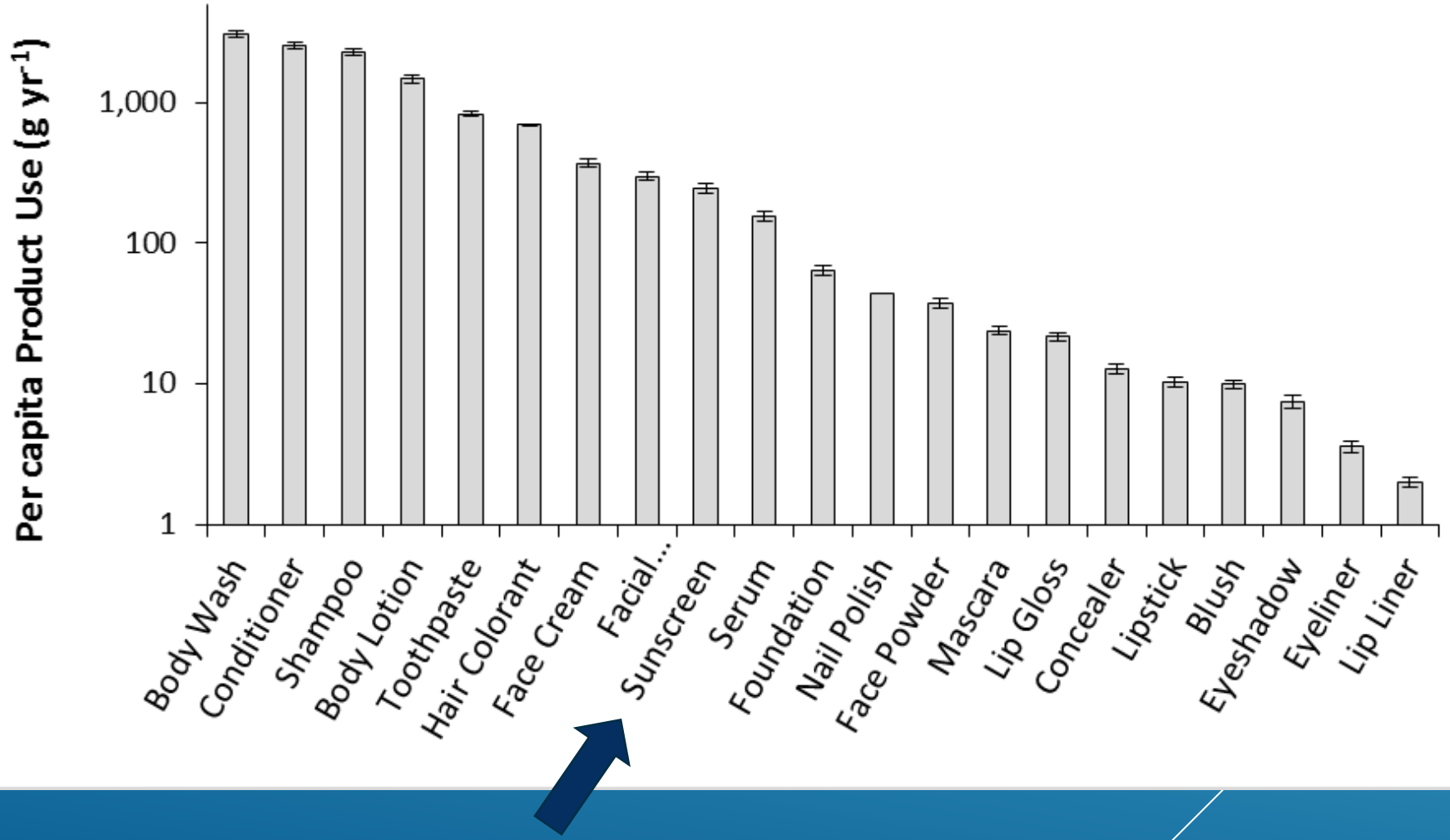


Source: Chemical Communications: Chem. Commun., 2006, 941-949



Source: Antaria Nanotechnologies http://www.antaria.com/irm/content/nanotechnology.aspx

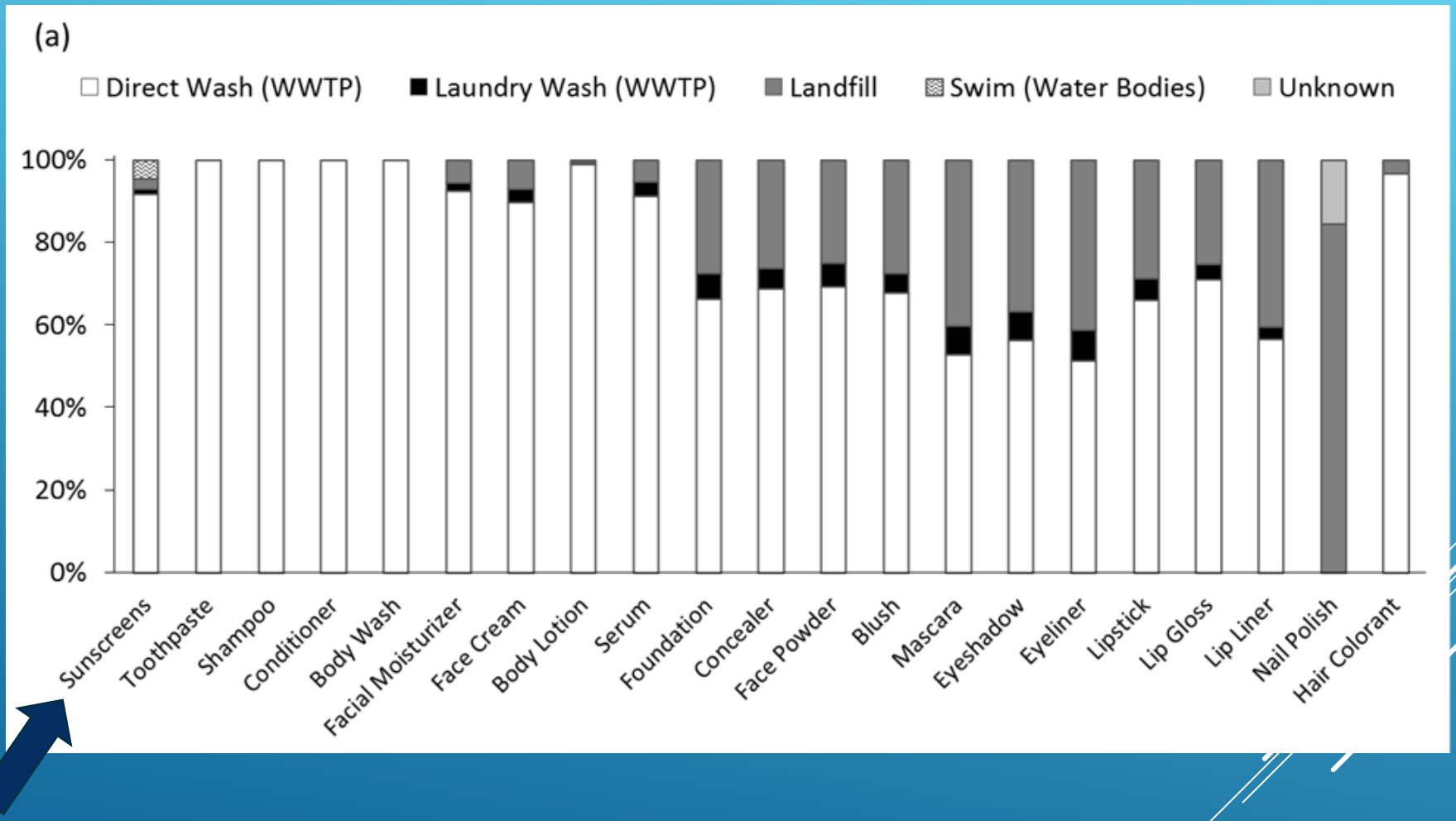
HOW MUCH SUNSCREEN DO WE USE?



N = 495

Keller, Vosti et al., JNR 2014 (doi:10.1007/s11051-014-2489-9)

Where does it end up?



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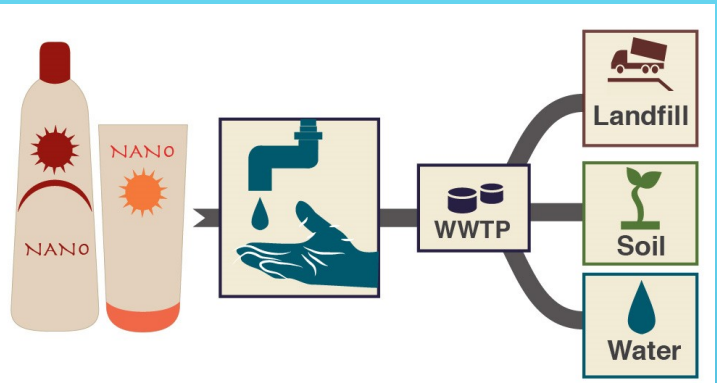
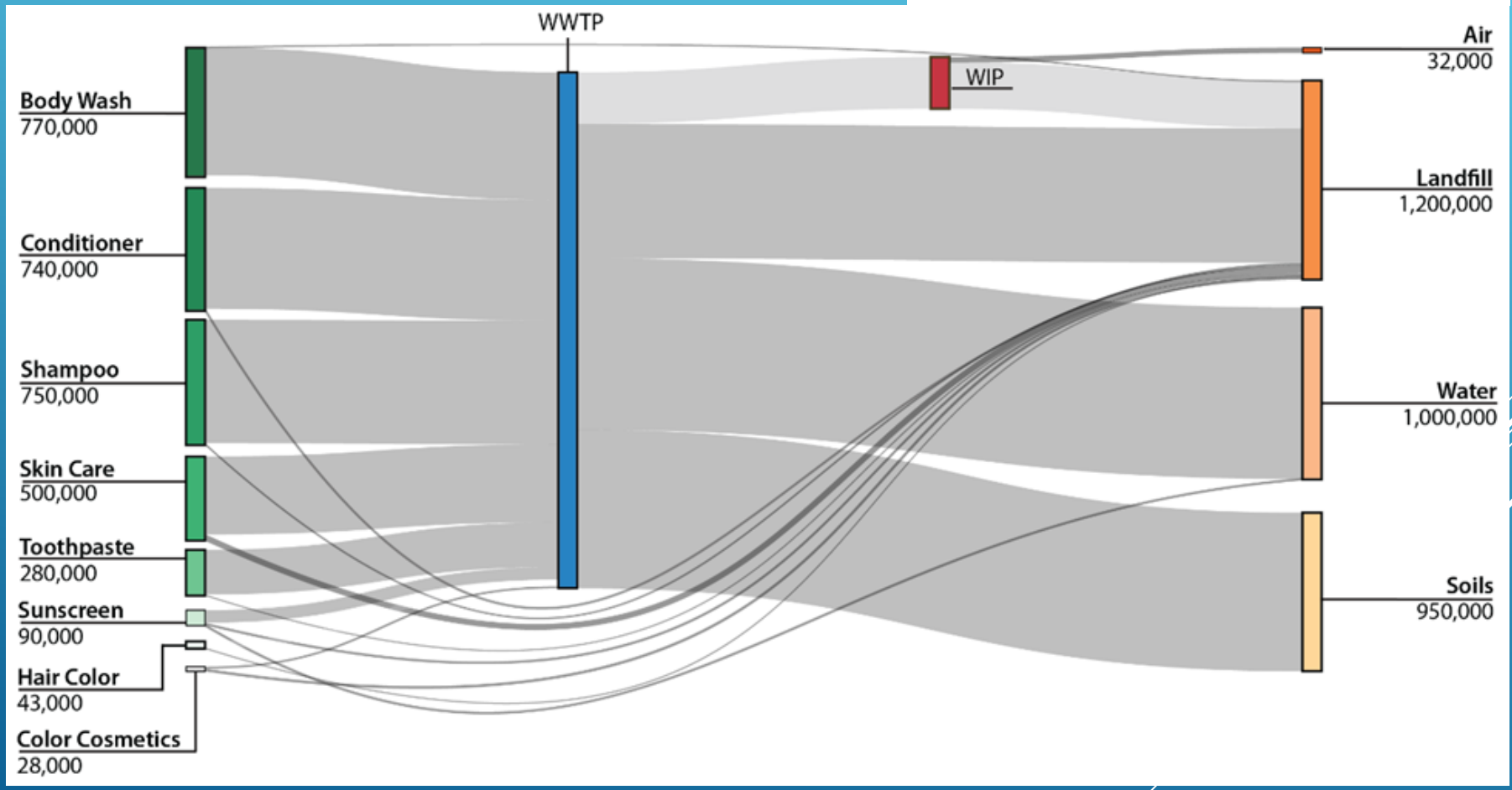
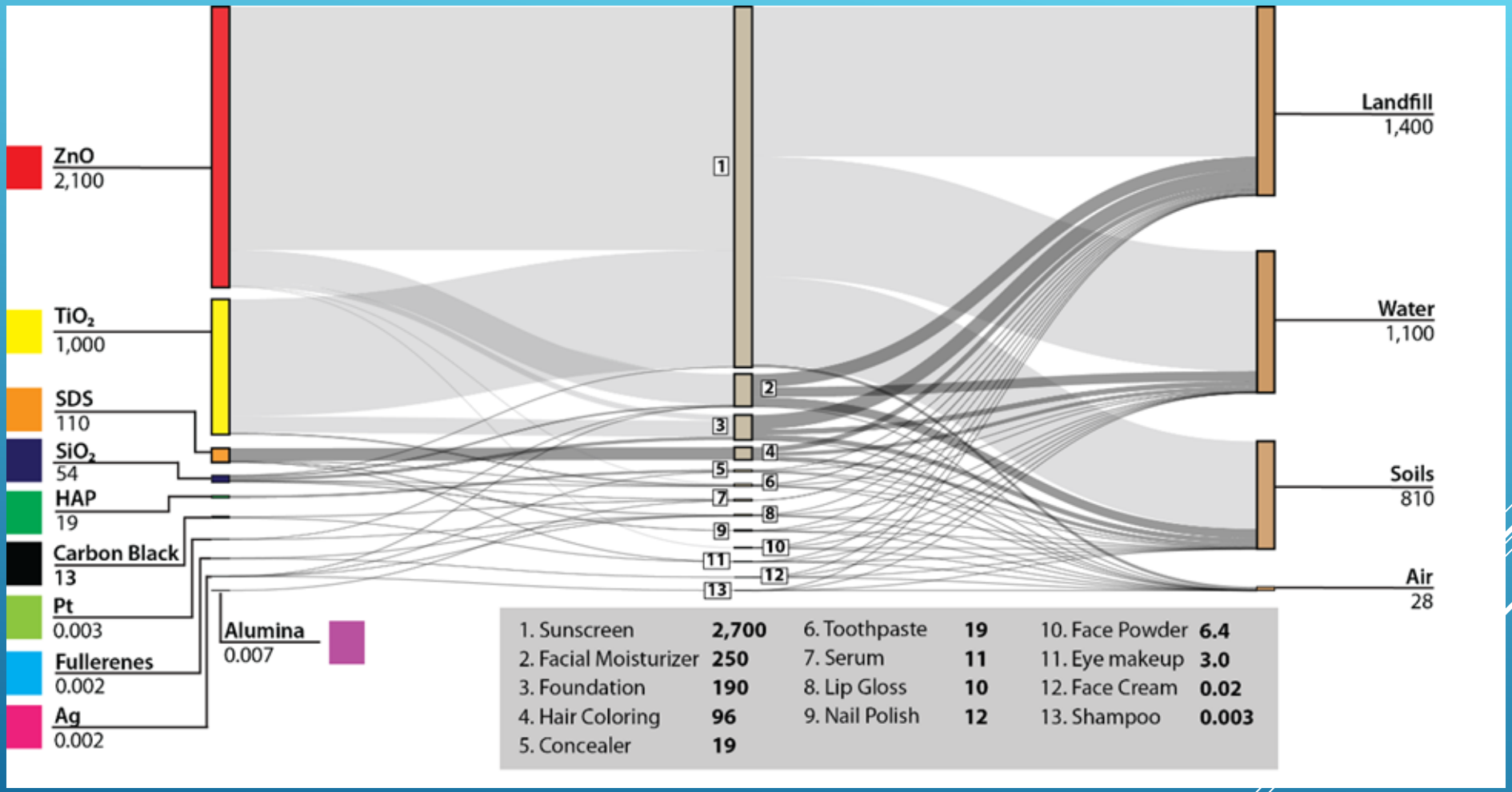




US Annual material flows in m ton/yr

Keller, Vosti et al., JNR 2014 (doi)

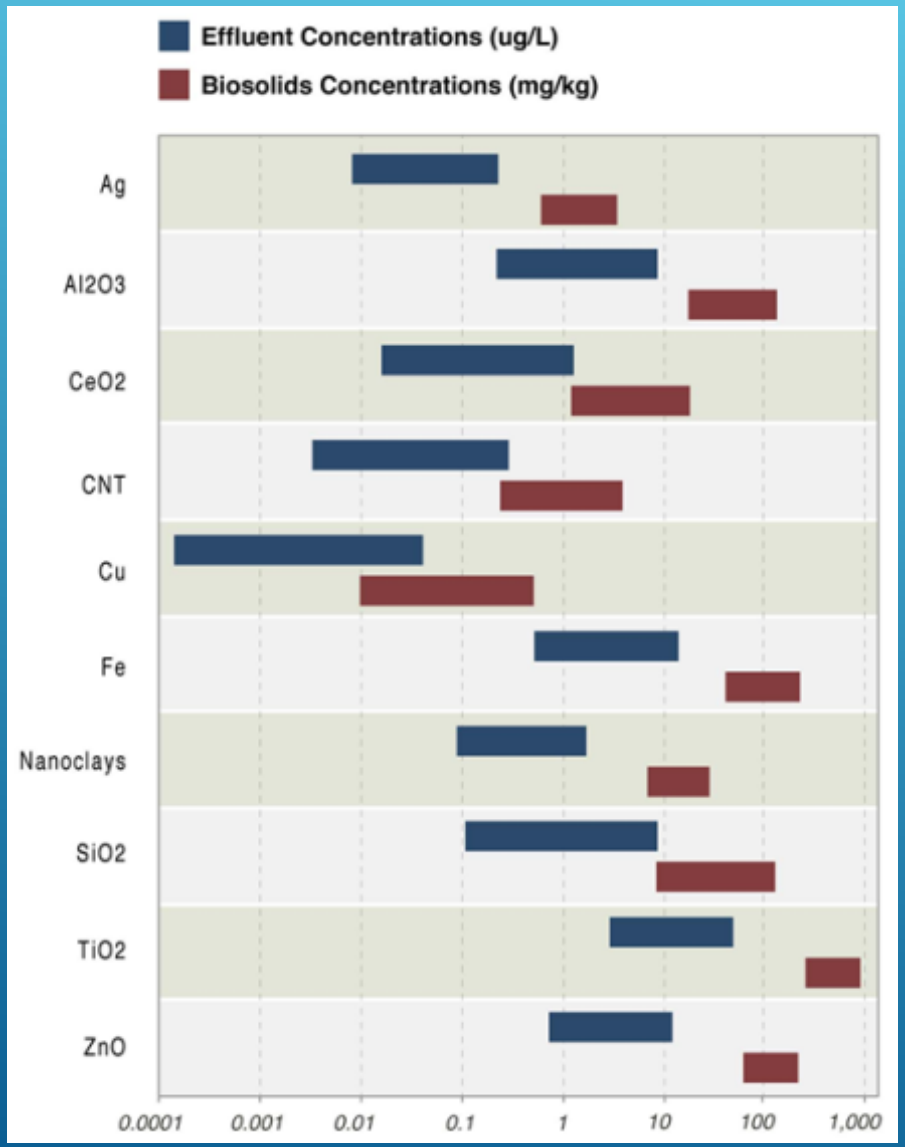
How much is nano? What type of nano?



US Annual material flows in m ton/yr

Keller, Vosti et al., JNR 2014 (doi)

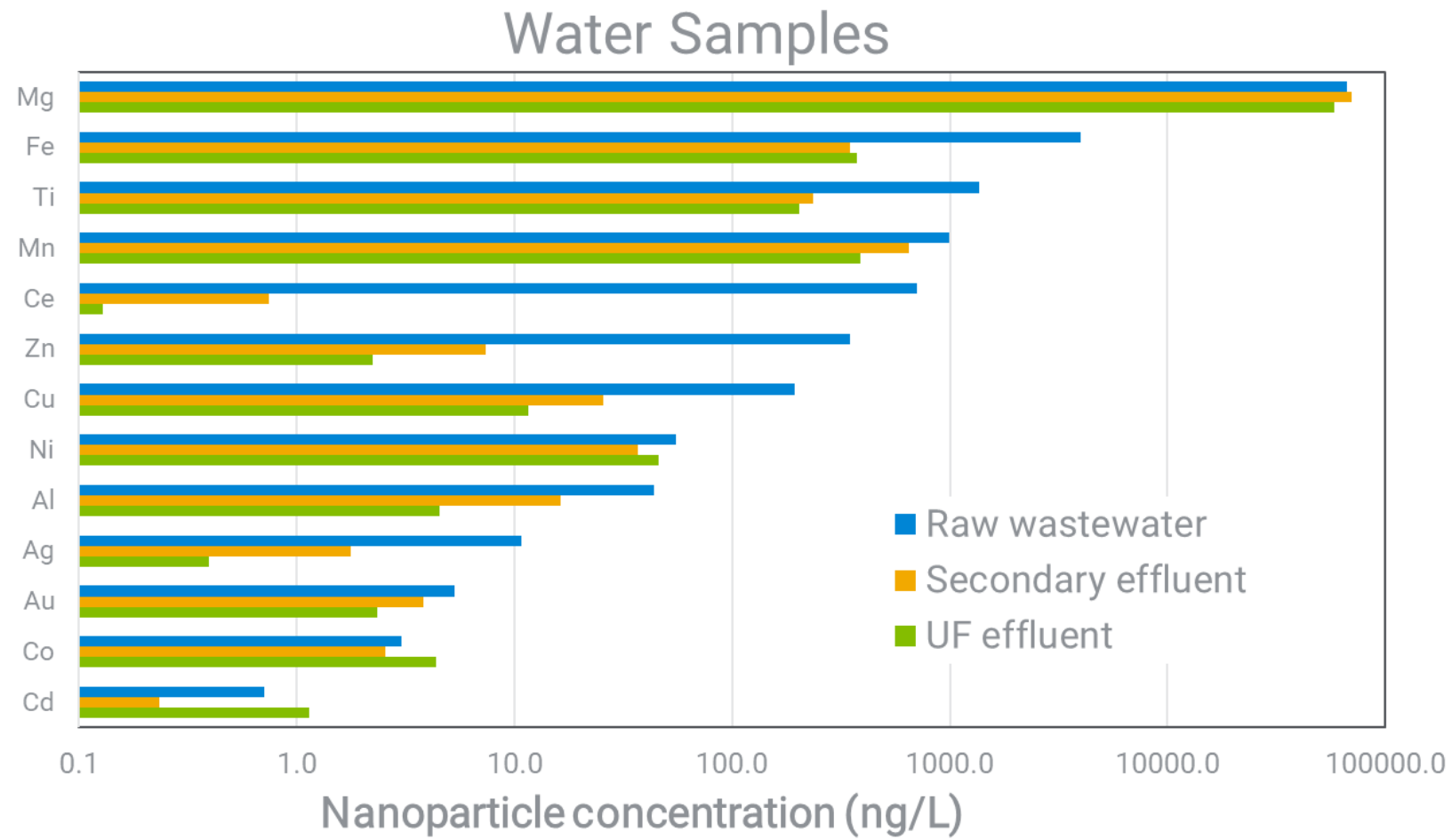
Predicted concentrations after WWTPs



Estimates of ENM concentrations at point of release indicate ng/L to ug/L levels to be expected

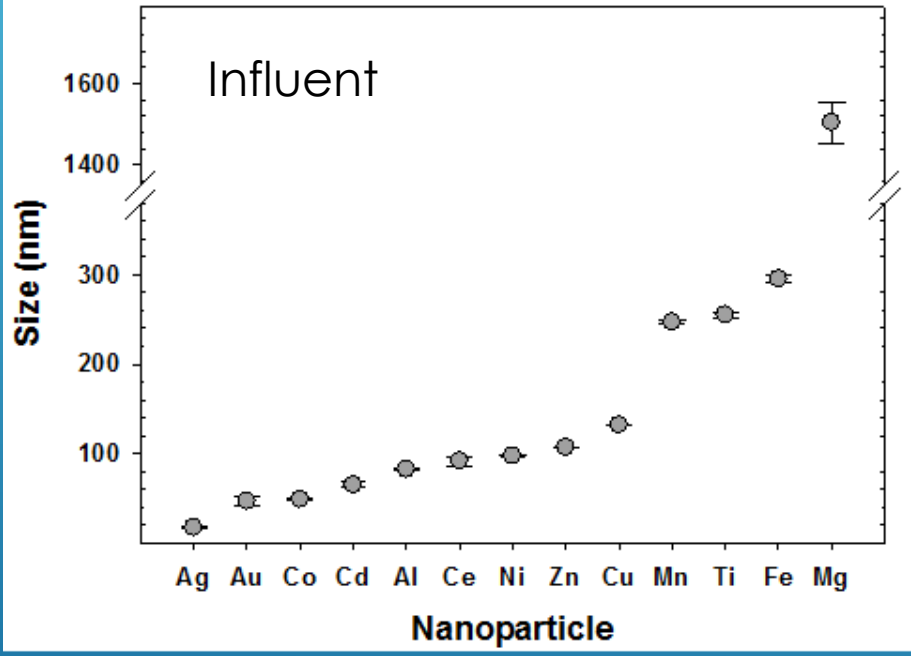
Lazareva and Keller, ACS Sus Chem, 2014

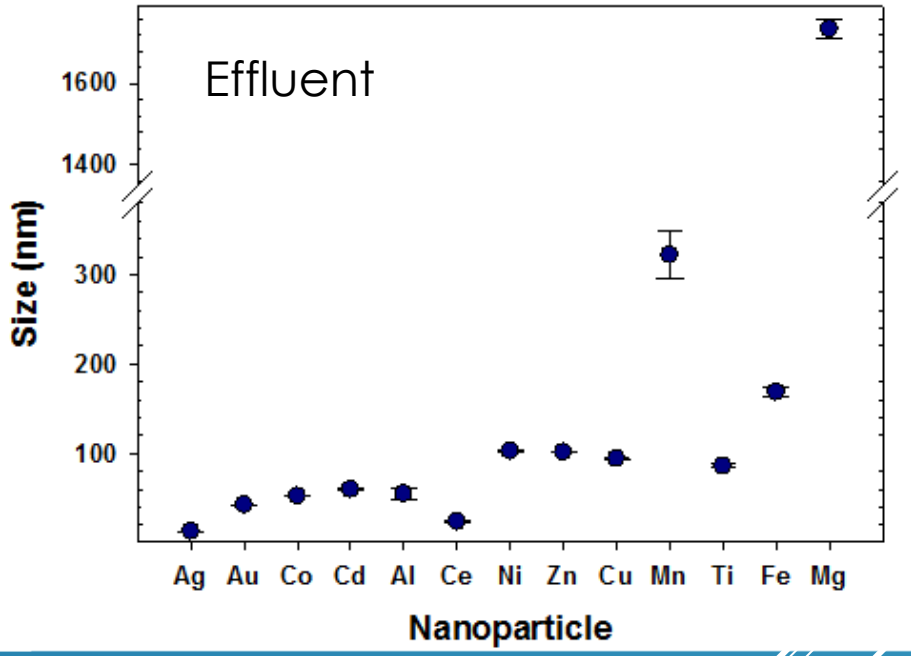
Nano in Treated Wastewater



Huang, Keller et al., ACS ES&T Water 2021 doi: 10.1021/acsestwater.0c00083

NP size in Treated Water Streams





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FATE & TRANSPORT PROCESSES

ENM-Environment Interactions

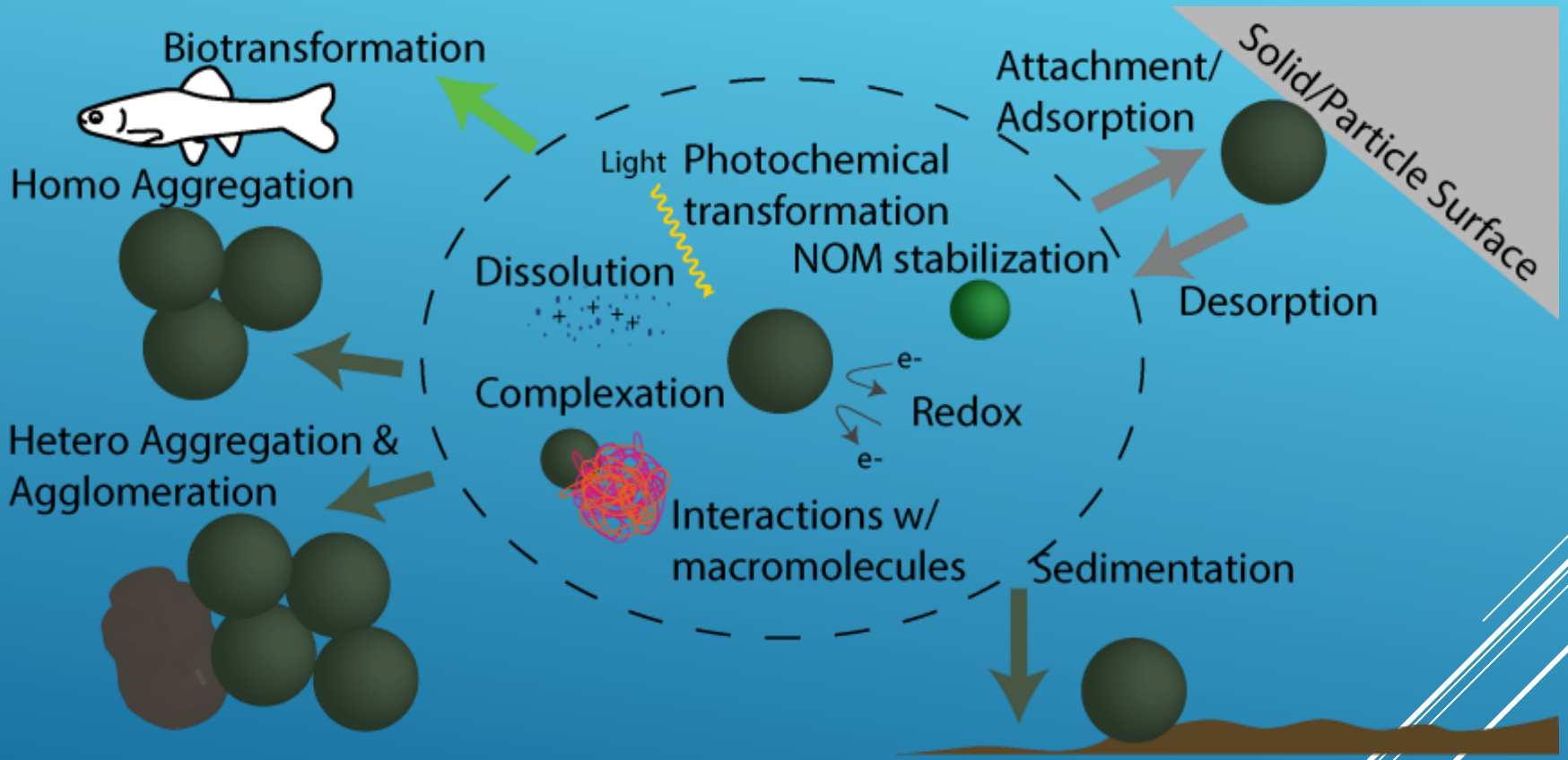


Figure from: Garner and Keller, JNR 2014

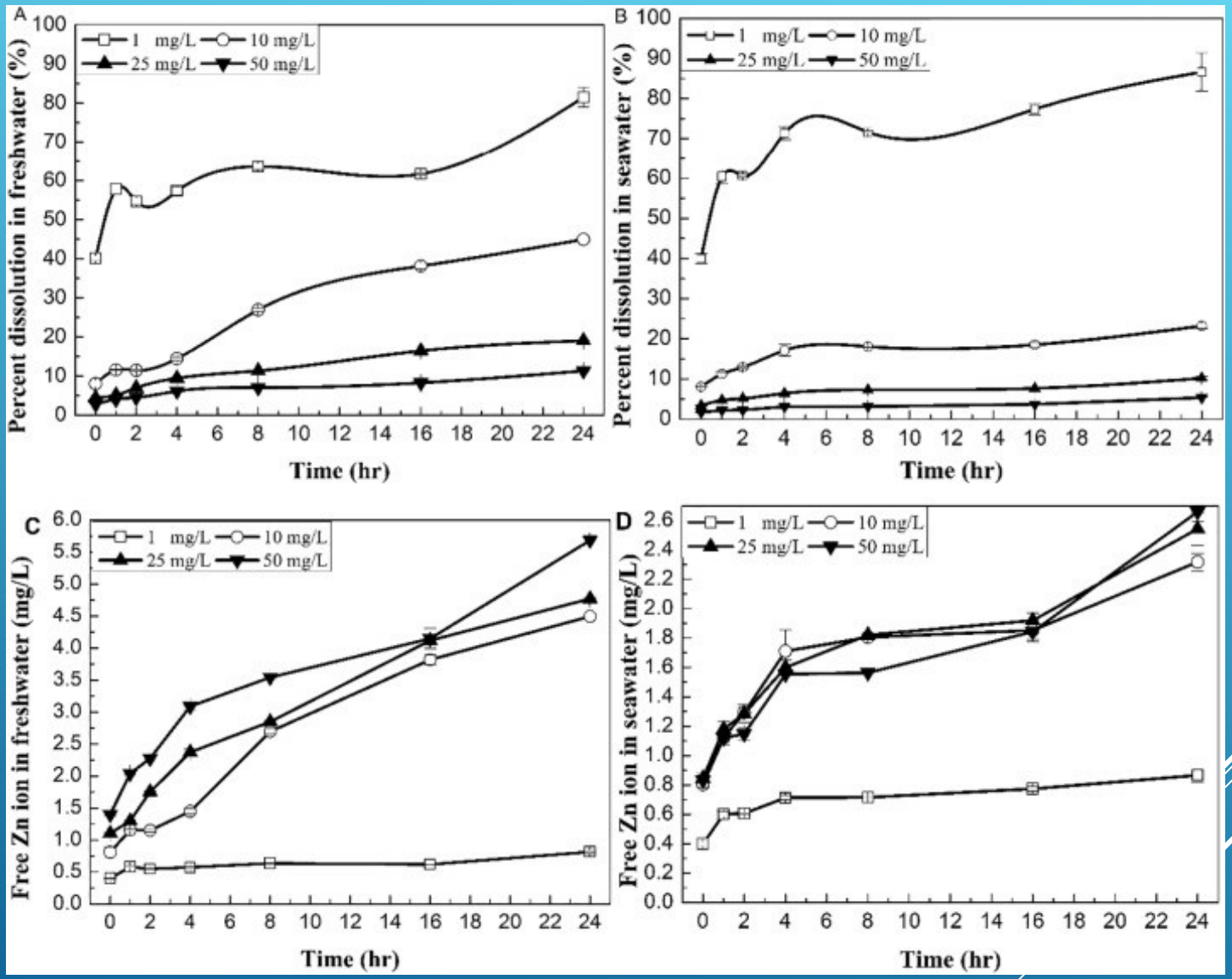
Process Rates from literature

Process	Environment	CeO_2	CuO	TiO_2	ZnO
Heteroaggregation	Freshwater				
	Marine				
Sedimentation	Freshwater				
	Marine				
Dissolution	Freshwater				
	Marine				
	Soil Water				

None Slow Medium Fast Very Fast Extremely Fast

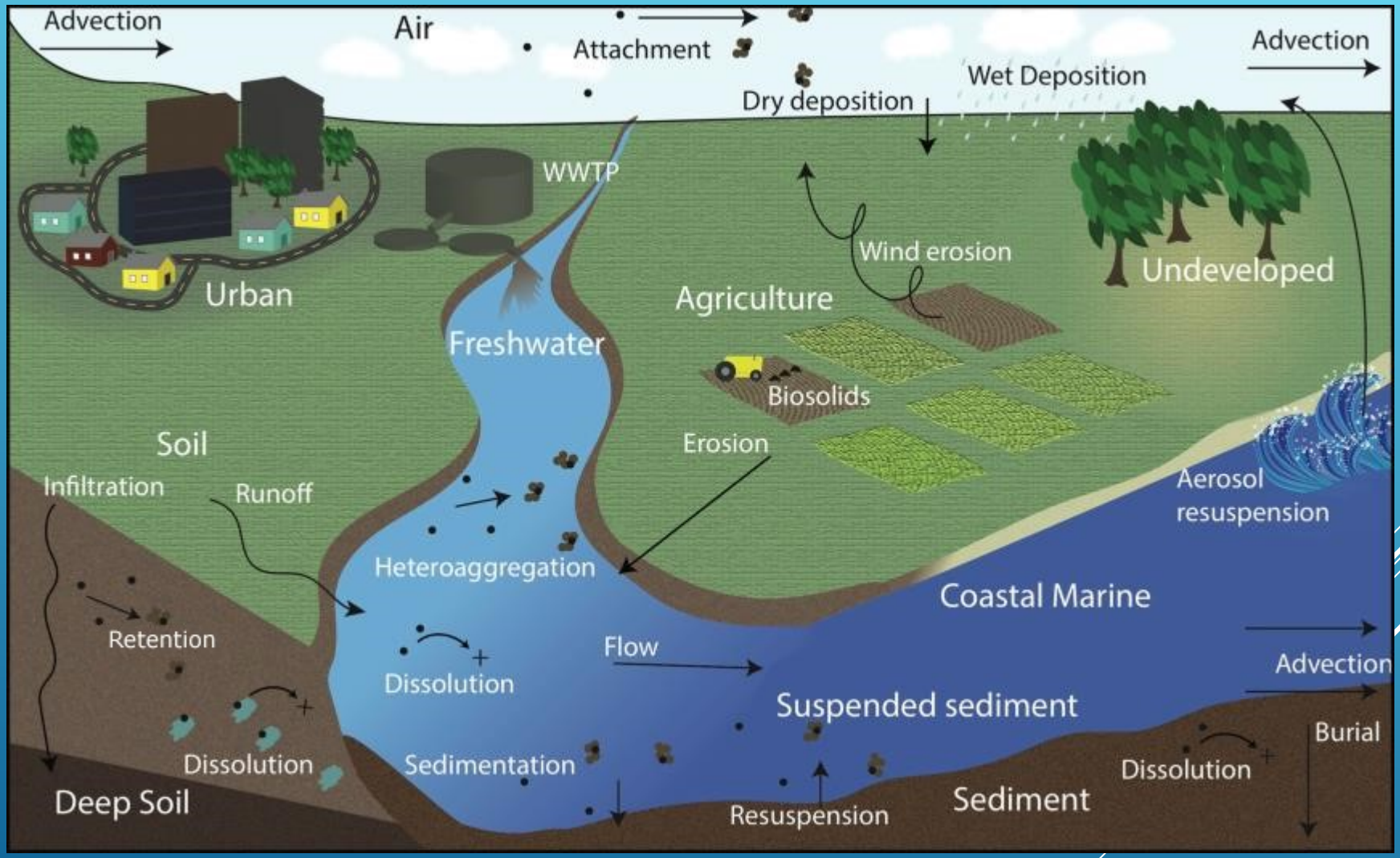
Garner, Keller et al., JNR 2014

Fast Dissolution of ZnO



Li, Chen et al., J Env. Sci 2018 (doi = 10.1016/j.jes.2018.01.015)

nanoFate Model

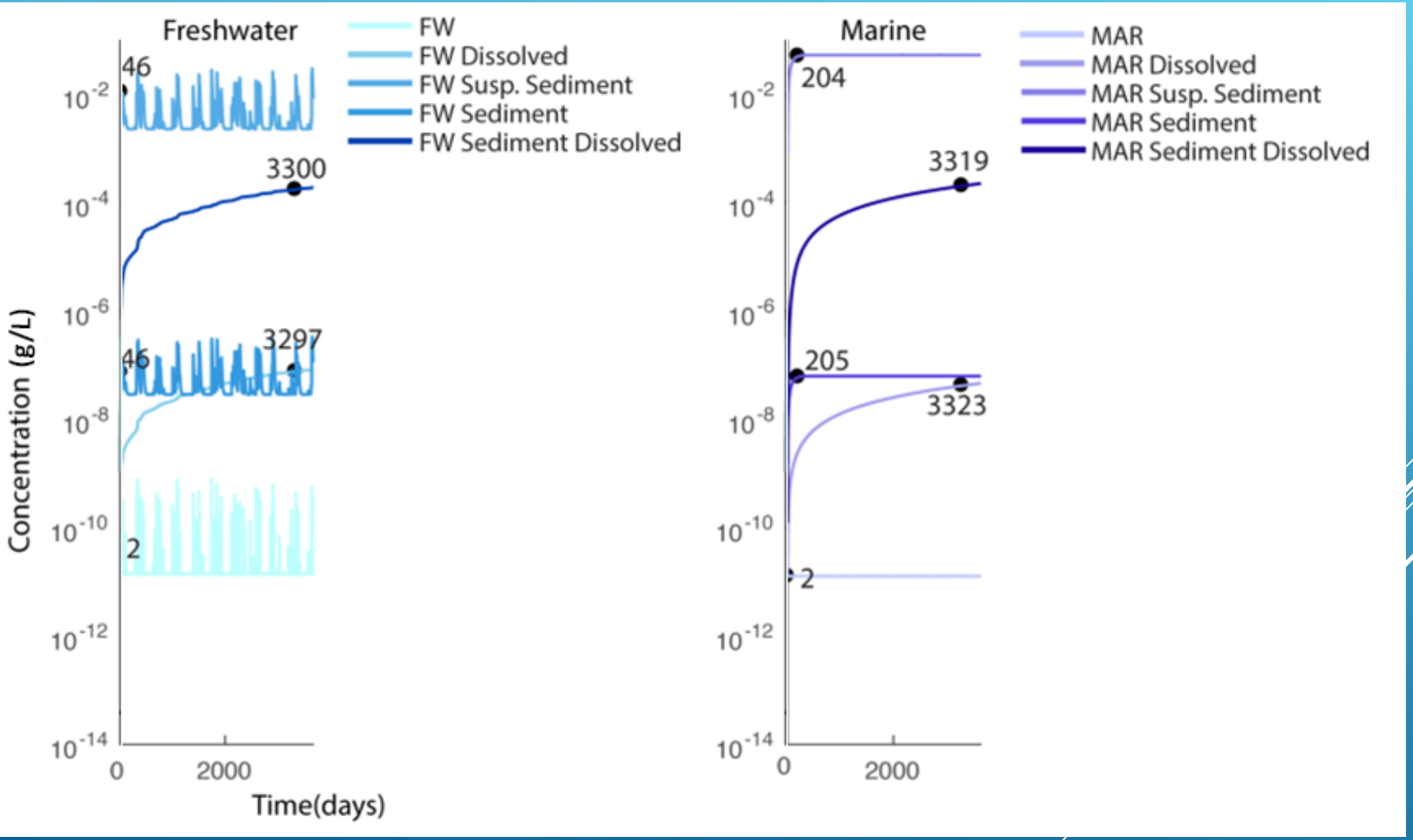


Freely available in GitHub

Garner, Keller et al., ES&T 2017, doi:10.1021/acs.est.6b05279

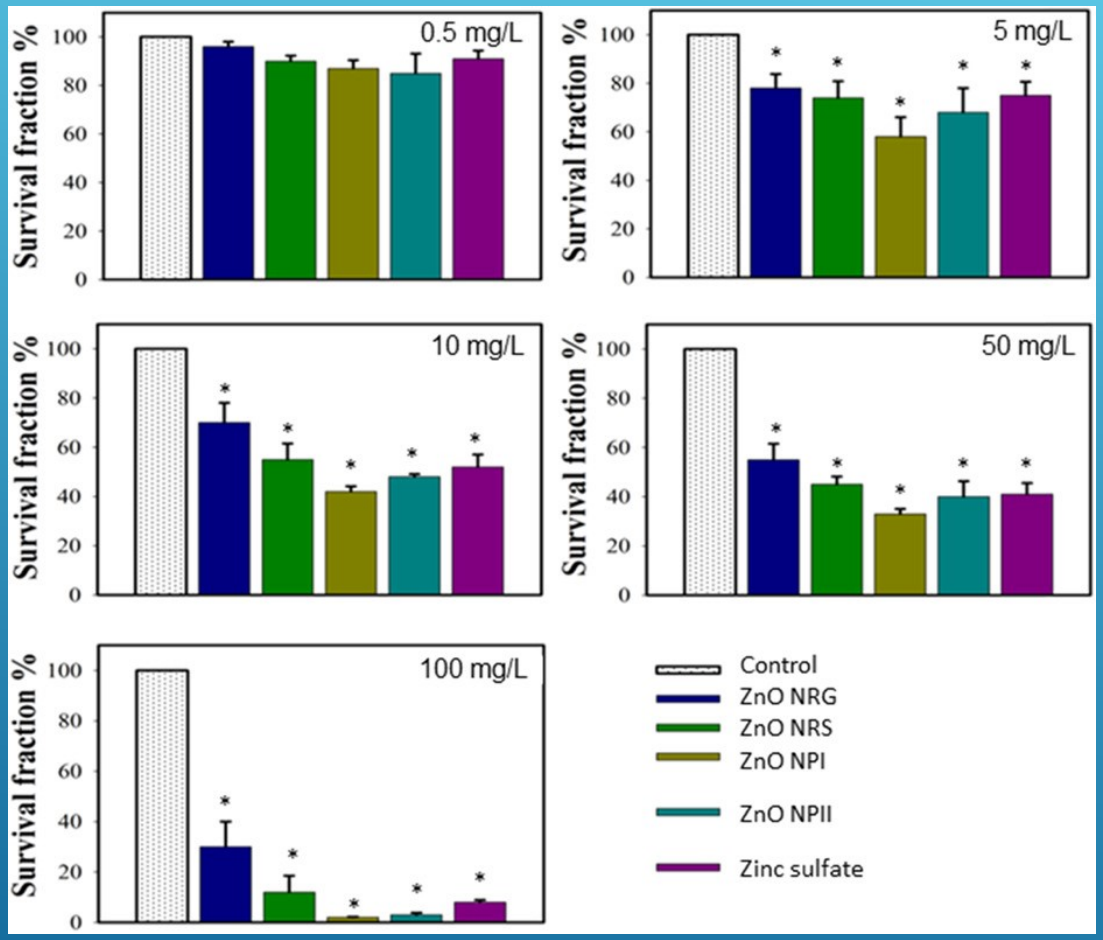
ZnO Concentrations

Assuming ZnO enters as ENM to all compartments



Garner, Keller et al., ES&T 2017, doi:10.1021/acs.est.6b05279

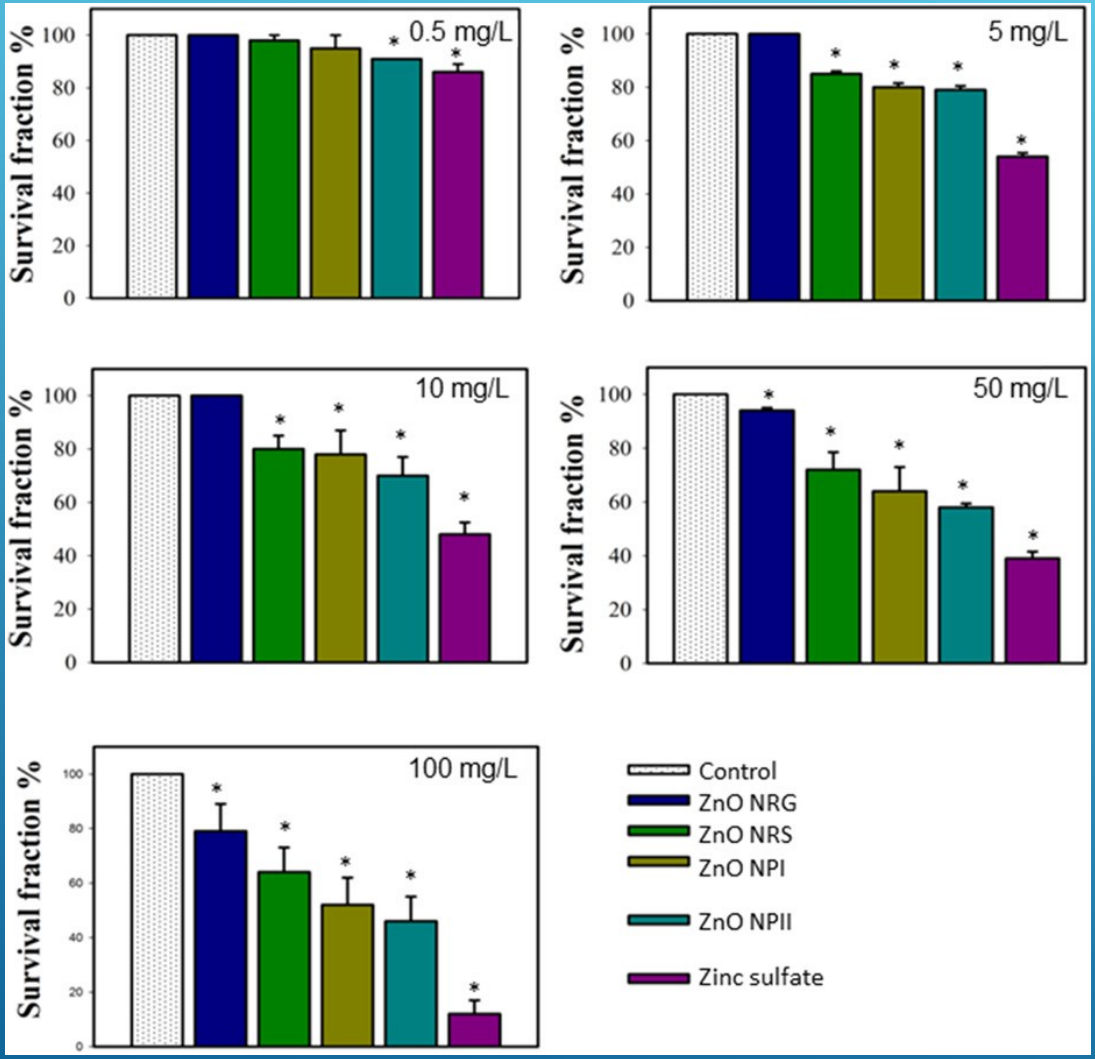
Toxicity of zinc oxide (ZnO) nanostructures to *Artemia salina* (brine shrimp) larvae after 24h



- ZnONPI = ZnO nanoparticles of 10 to 30 nm;
- ZnONPII = ZnO nanoparticles of 80 to 200 nm;
- ZnONRG = ZnO nanorods supported on a glass substrate
- ZnONRS = nonsupported ZnO nanorods.

Dobretsov et al. Env Tox & Chem 2020 (doi: 10.1002/etc.4720)

Toxicity of zinc oxide (ZnO) nanostructures to *Dunaliella salina* (green micro-algae) after 24h



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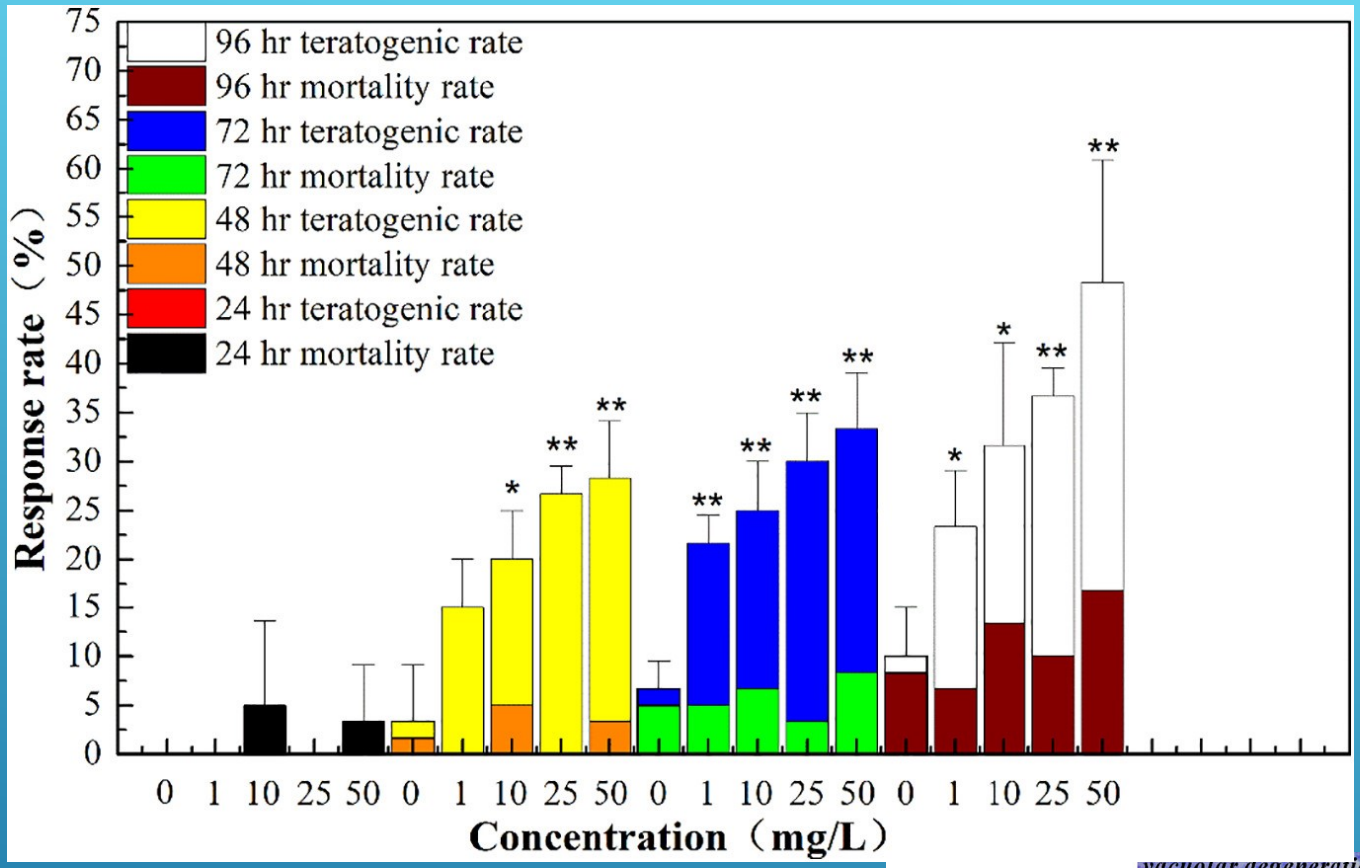
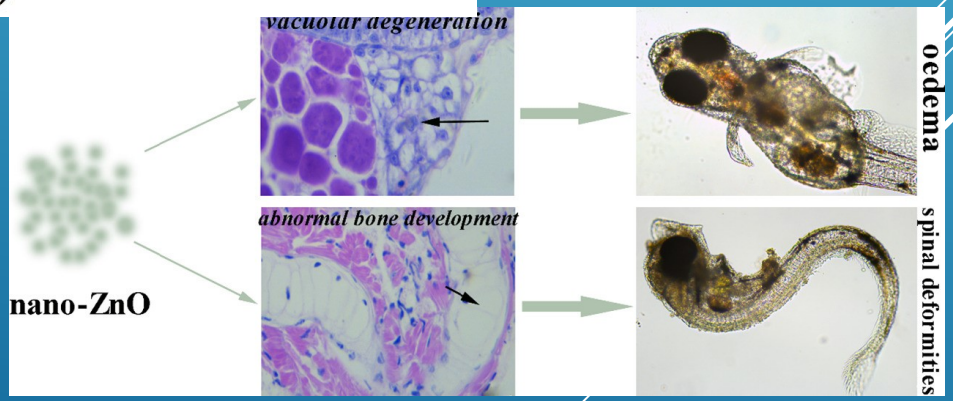


Yellowstriped goby
(*Mugilogobius chulae*)



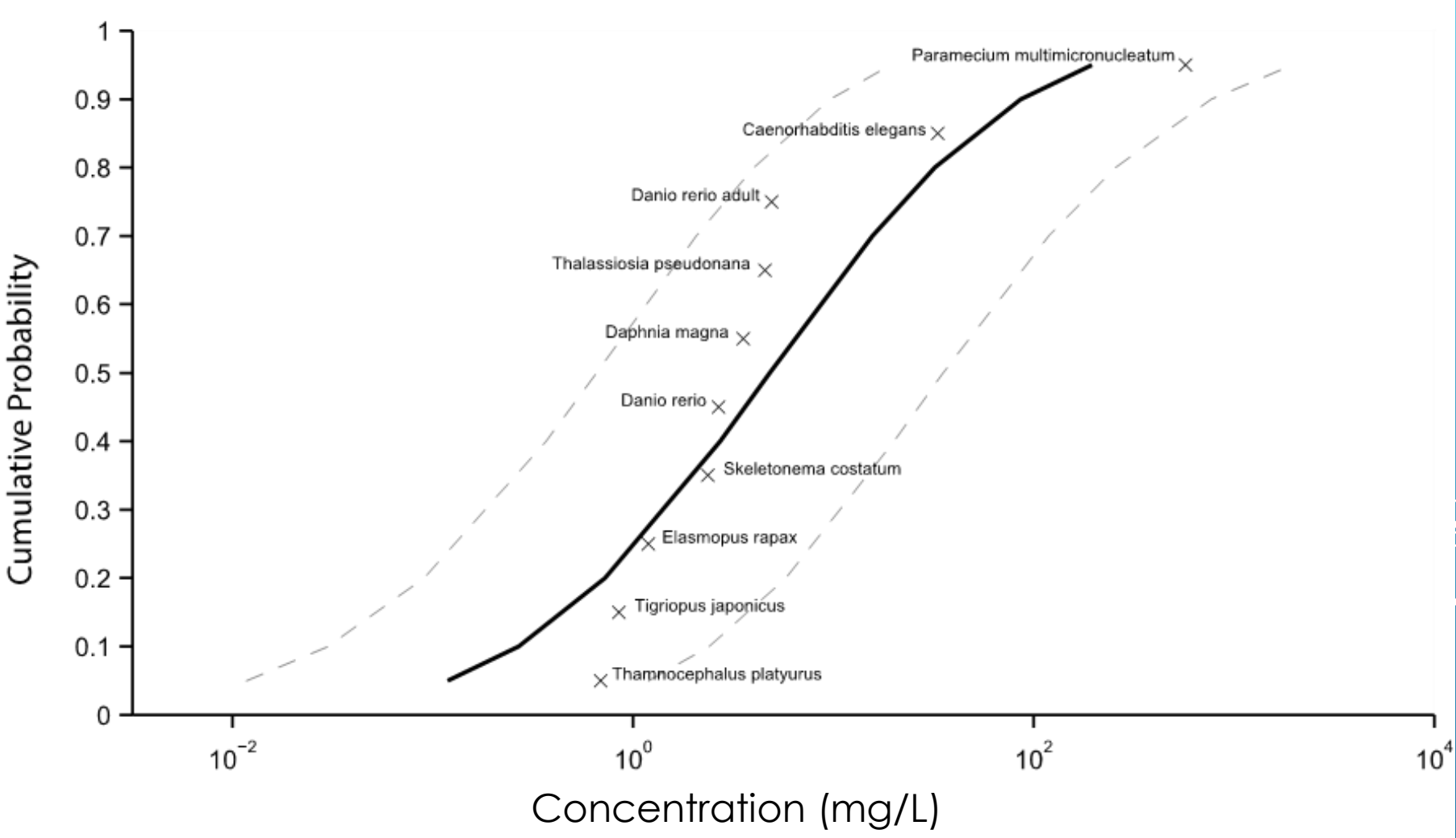
Li, Chen et al., J Env. Sci 2018 (doi:10.1016/j.jes.2018.01.015)

Ecotoxicity

	Biological species	Exposure time	Range studied	EC50 (μg/L) in lethality (size)	Reference
Nano-TiO2	Nitzschia closterium (marine species)	96 h	5–100 mg/L 10–360 mg/L 20–500 mg/L	88.78 mg/L (21 nm) 118.80 mg/L (60 nm) 179.05 mg/L (400 nm) 2.36 mg/L nano	Xia et al. (2015)
	Phaeodactylum tricornutum (marine species)	5 days	5–200 mg/L	167.71 mg/L	Wang et al. (2016c)
	Chlorella pyrenoidosa	96 h	0.1–20 mg/L (anatase)	9.1 mg/L	Middepogu et al. (2018)
ZnO	Chlamydomonas reinhardtii	8 days	1–100 mg/L	≥ 0.01 mg/L	Gunawan et al. (2013)
	Skeletonema costatum	24 h 48 h 72 h 96 h	5–50 mg/L	7.0 mg/L 6.4 mg/L 4.4 mg/L 3.6 mg/L	Zhang et al. (2016a)
	Phaeodactylum tricornutum (marine diatom)	24 h 48 h 72 h	0.1–10 mg/L	2.57 mg/L nano 1.12 mg/L bulk 1.41 mg/L nano 3.32 mg/L bulk 1.09 mg/L nano 3.47 mg/L bulk	Li et al. (2017)

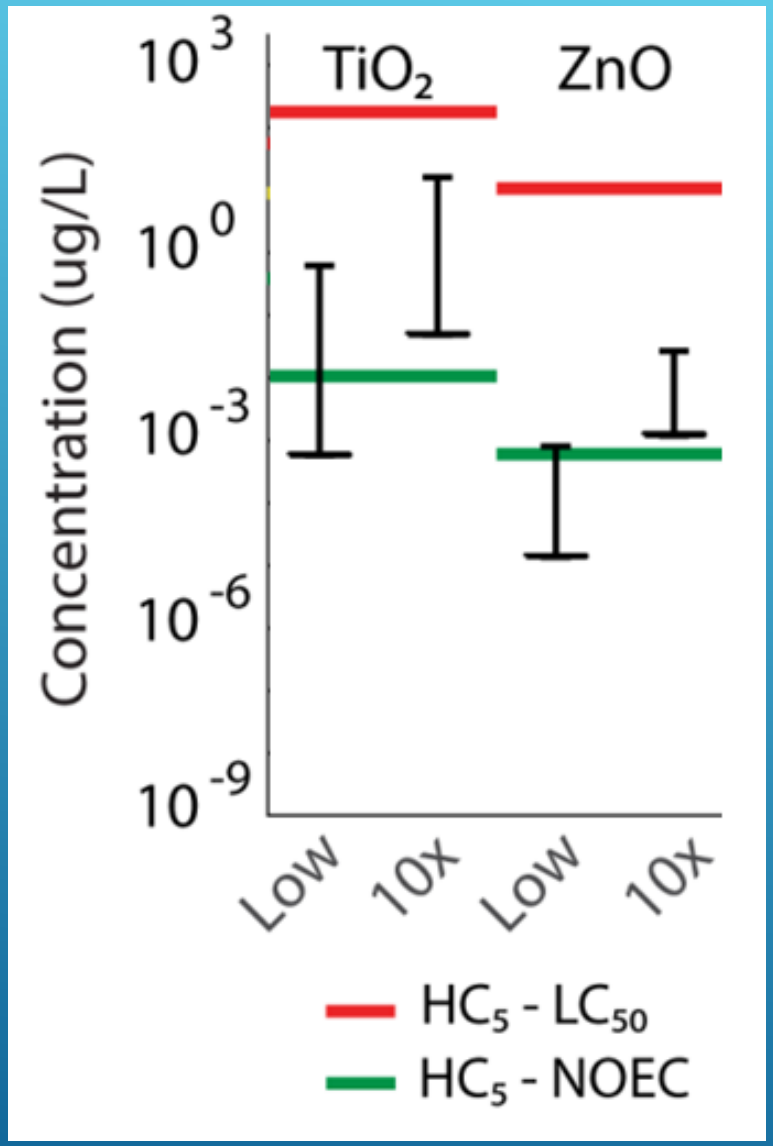
Xin et al., J Haz Matls 2021, doi:10.1016/j.jhazmat.2020.124619

nZnO Species Sensitivity Distribution



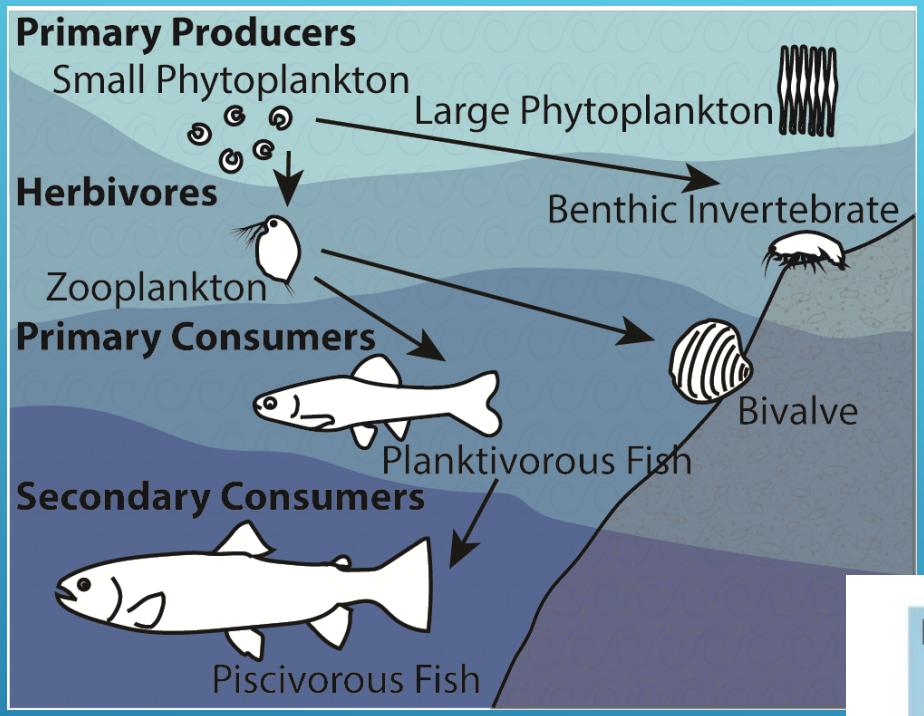
Garner, Keller et al., ES&T 2015 (doi: **10.1021/acs.est.5b00081**)

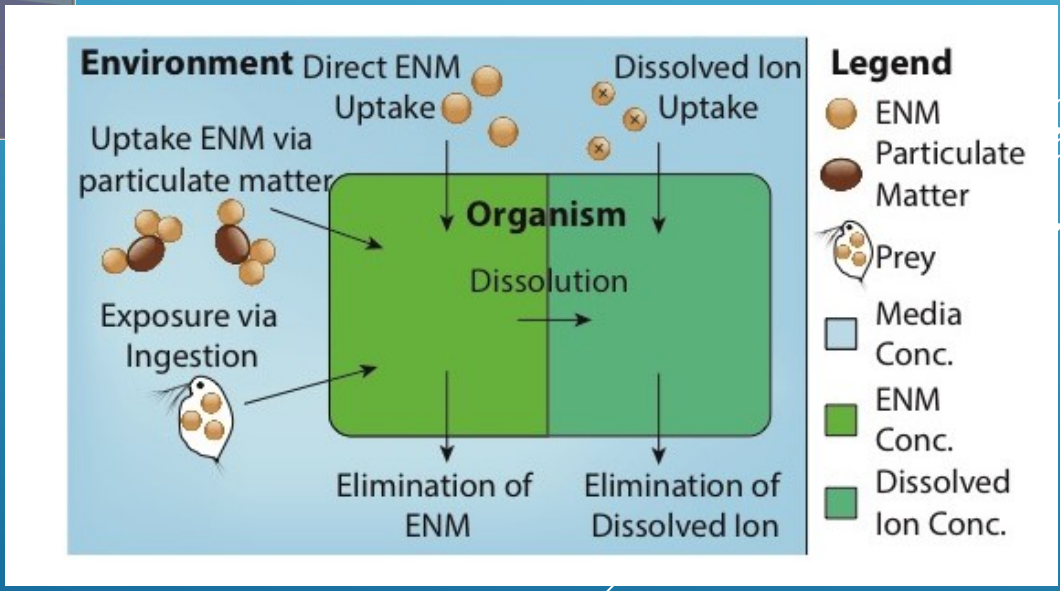
Relative Risk - Freshwater



Garner, Keller et al., ES&T 2017, doi:10.1021/acs.est.6b05279

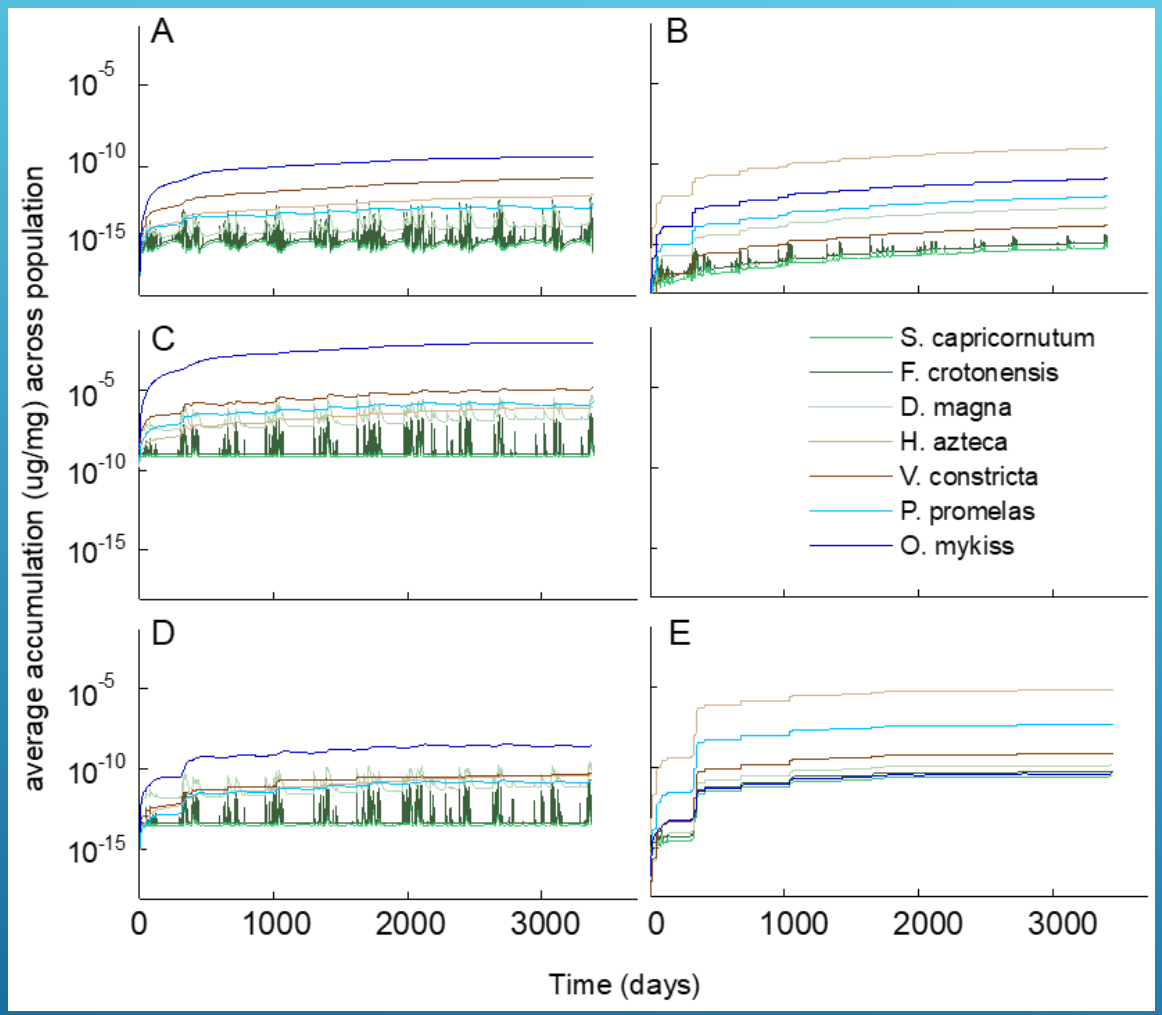
nanoBio(accumulation) model





Garner, Keller et al., ACS Sus Chem 2018, doi:10.1021/acssuschemeng.8b01691

Bioaccumulation of nZnO & $nTiO_2$



- Concentrations reflect average across population
- Longer-lived species accumulate more
- Dissolved Zn^{2+} concentrations continue to increase even after 10 years

(A) nCuO, (B) dissolved Cu^{+2}, (C) $nTiO_2$, (D) nZnO, and (E) dissolved Zn^{+2} in simple food chain

Garner, Keller et al., ACS Sus Chem 2018, doi:10.1021/acssuschemeng.8b01691

KEY POINTS

- Nano ZnO and TiO_2 provide useful screening of UV
- Most sunscreens applied and washed off within hours
- Largest fraction goes to wastewater; some direct release to freshwater bodies and coastal areas
- Nanoparticles are transformed in treatment plant, yet a fraction still released as nano
- ZnO mostly released as dissolved Zn^{2+}
- In environment, NPs mostly removed by aggregation into larger particles that deposit
- ZnO is considerably more toxic to aquatic organisms than TiO_2
- During peak release/resuspension events, concentrations of nanoTiO_2 may be above toxicity thresholds

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Agilent Thought Leadership award

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+ many other students & colleagues

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