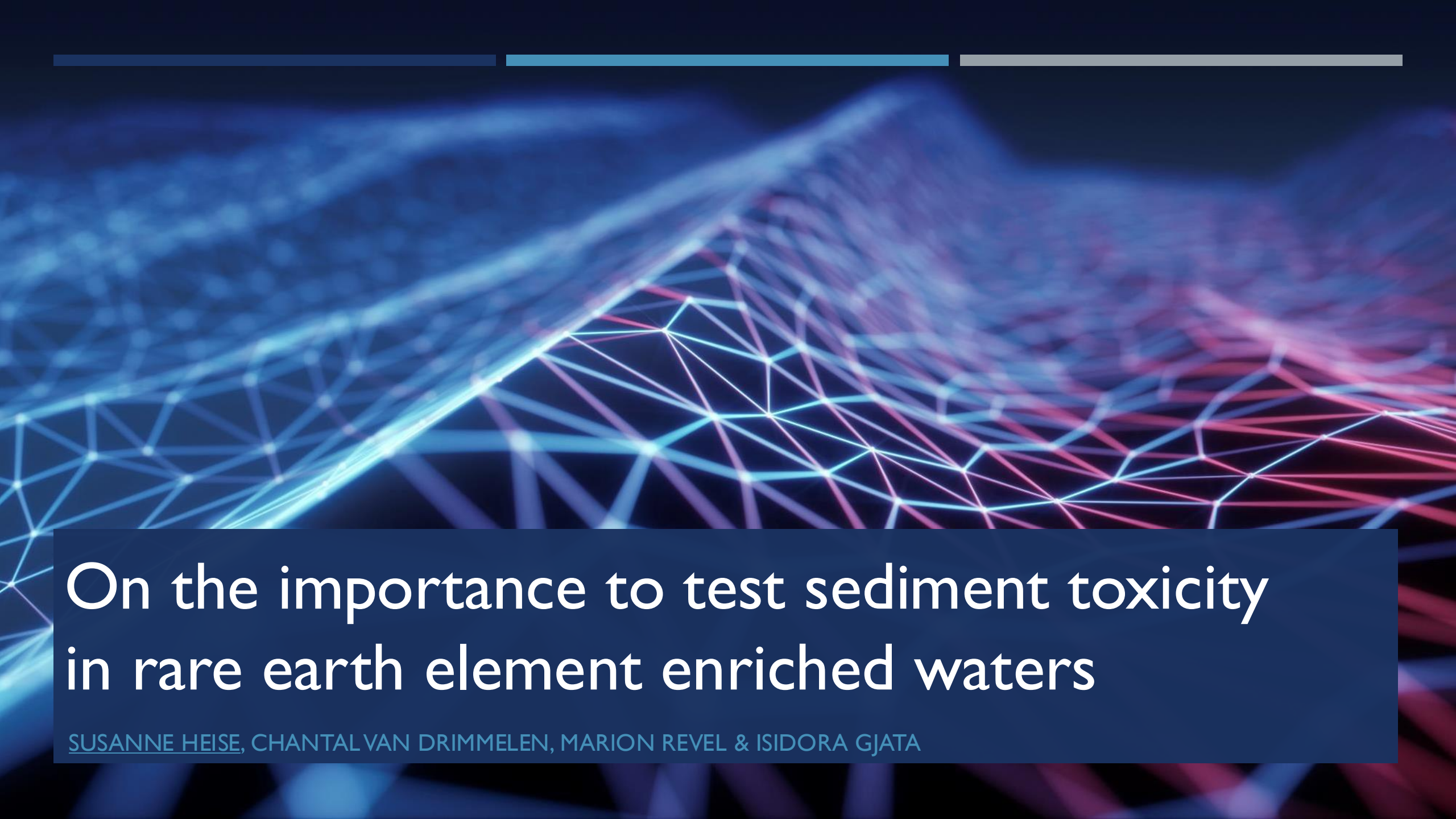


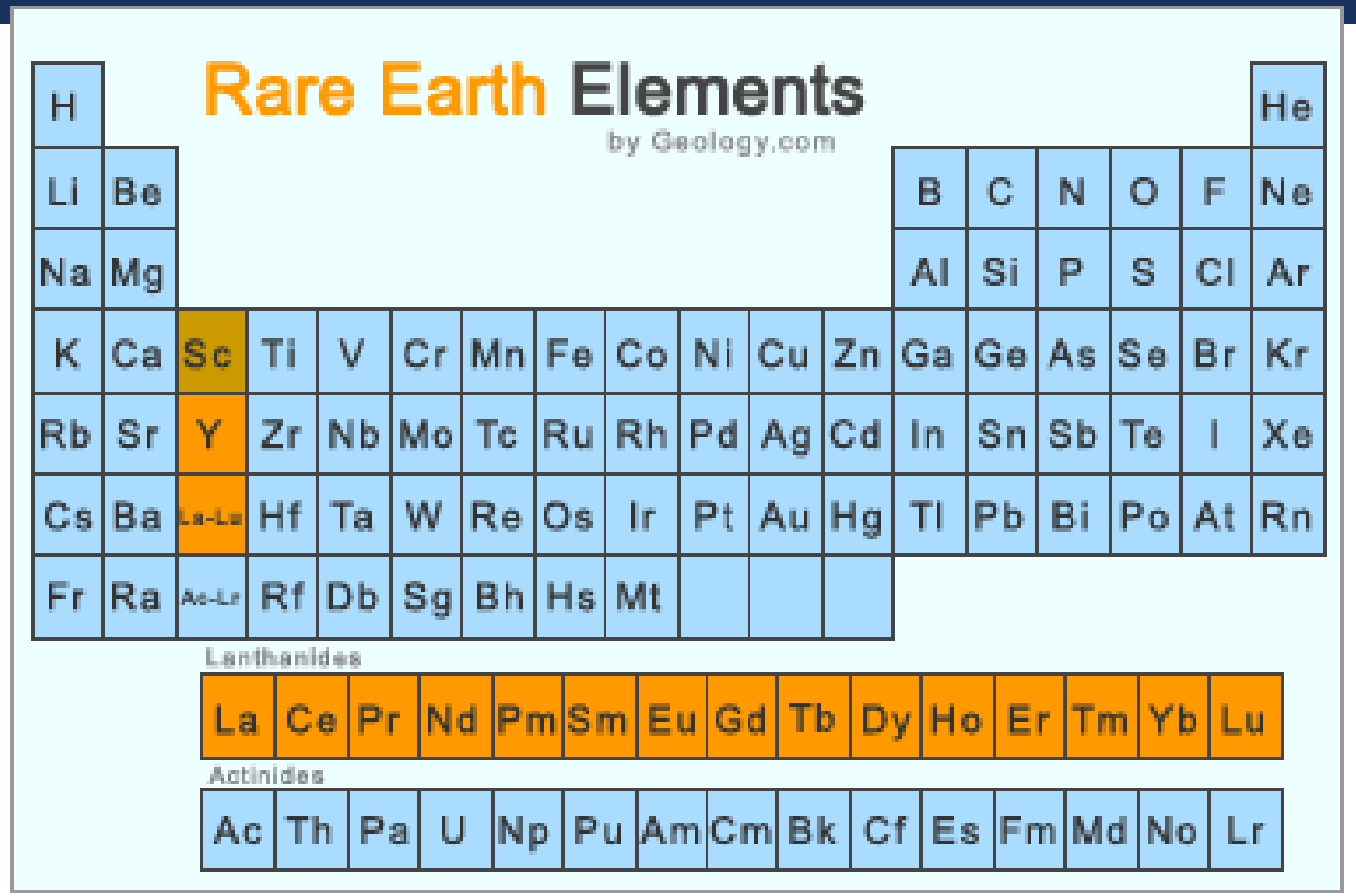
On the importance to test sediment toxicity in rare earth element enriched waters

SUSANNE HEISE, CHANTAL VAN DRIMMELEN, MARION REVEL & ISIDORA GJATA

Structure

- What are rare earth elements (REE)?
- Why do they occur in waters at elevated concentrations?
- What determines their fate in the environment?
- Are they toxic?
- Why should sediments be in focus?
- What are the next steps?

Rare Earth Elements (REE)



A group of 17 chemically similar elements:

Lanthanides plus and yttrium and scandium

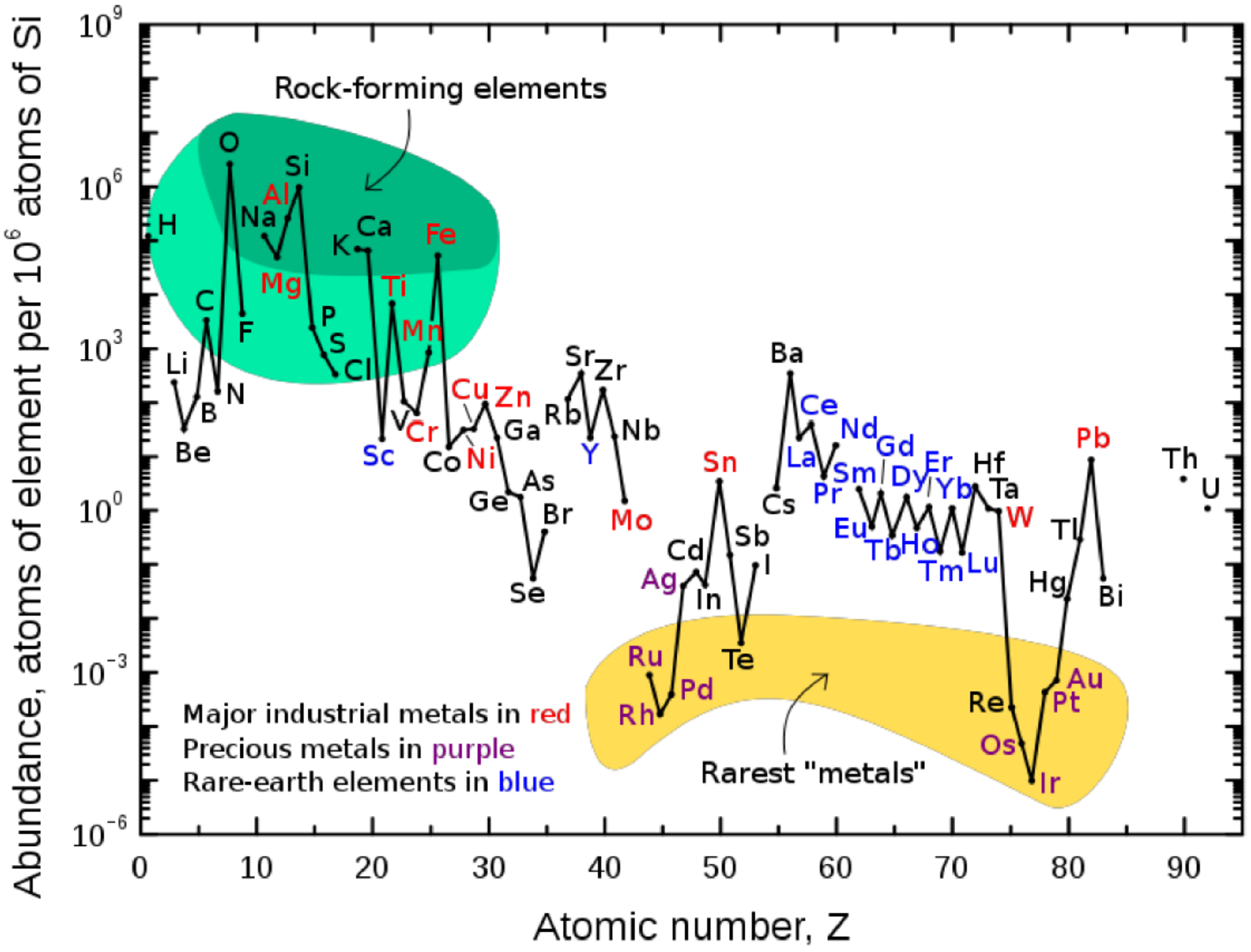
Are Rare Earth Metals …. rare?

Not really.

→ widespread

→ but occurr in low concentrations.

→ Technology Critical Elements (TCE)



Arienzo, M., Ferrara, L., Trifuoggi, M., Toscanesi, M. (2022); Water 14, 401

Reported anthropogenic anomalies in water bodies

River / Water Bodies	Country	REE	Source
Weser	Germany	Gd	Kulaksiz & Bau, 2007
Rhine	Germany	La, Sm, Gd, Ce	Kulaksiz & Bau, 2013
Atibaia River	Brazil	Gd	de Campos & Enzweiler, 2016
San Francisco Bay	USA	Gd	Hatje et al. 2016
Hérault River	France	Gd	Rabiet et al. 2009
Teltow Channel	Germany	Gd	Knappe et al. 2005
Wupper	Germany	Gd	Bau & Dulski 1996
Rhine Estuary	The Netherlands	Nd, Pr, Sm	Bakkenist & van de Wiel 1995
Tagus Estuary	Portugal	Y	Brito et al. 2018
Tokio Bay	Japan	Gd	Nozaki et al. 2000

Tepe, N., Romero, M., Bau, M. (2014) Applied Geochemistry 45, 191-197.http://dx.doi.org/10.1016/j.apgeochem.2014.04.006

And so??

Applications of Rare Earth Elements

Unique properties:

Magnetic (Nd, Pr, Dy)

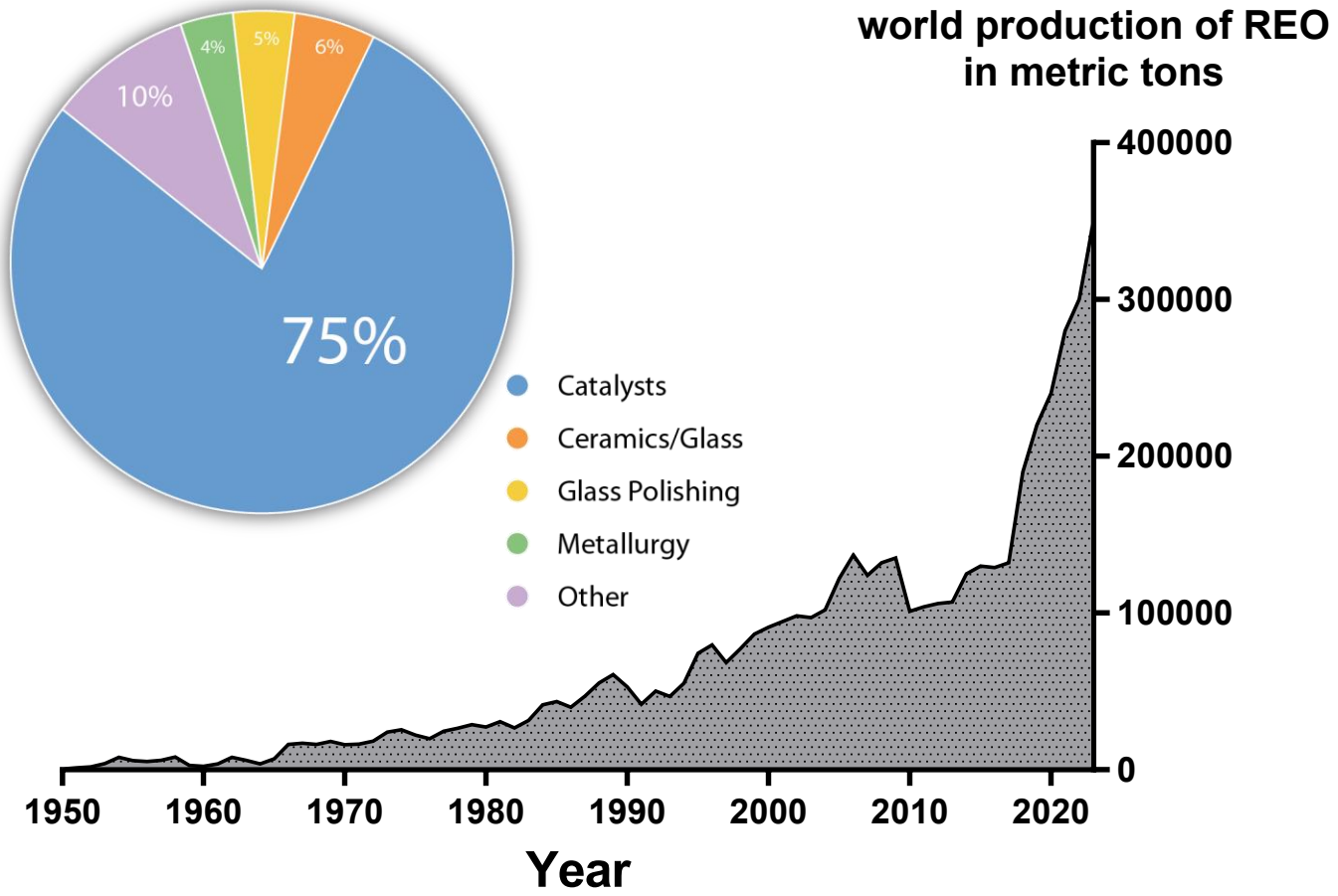
Optical (fluorescing – e.g. Eu)

Catalytical (La, Ce)

Thermic (Sm)

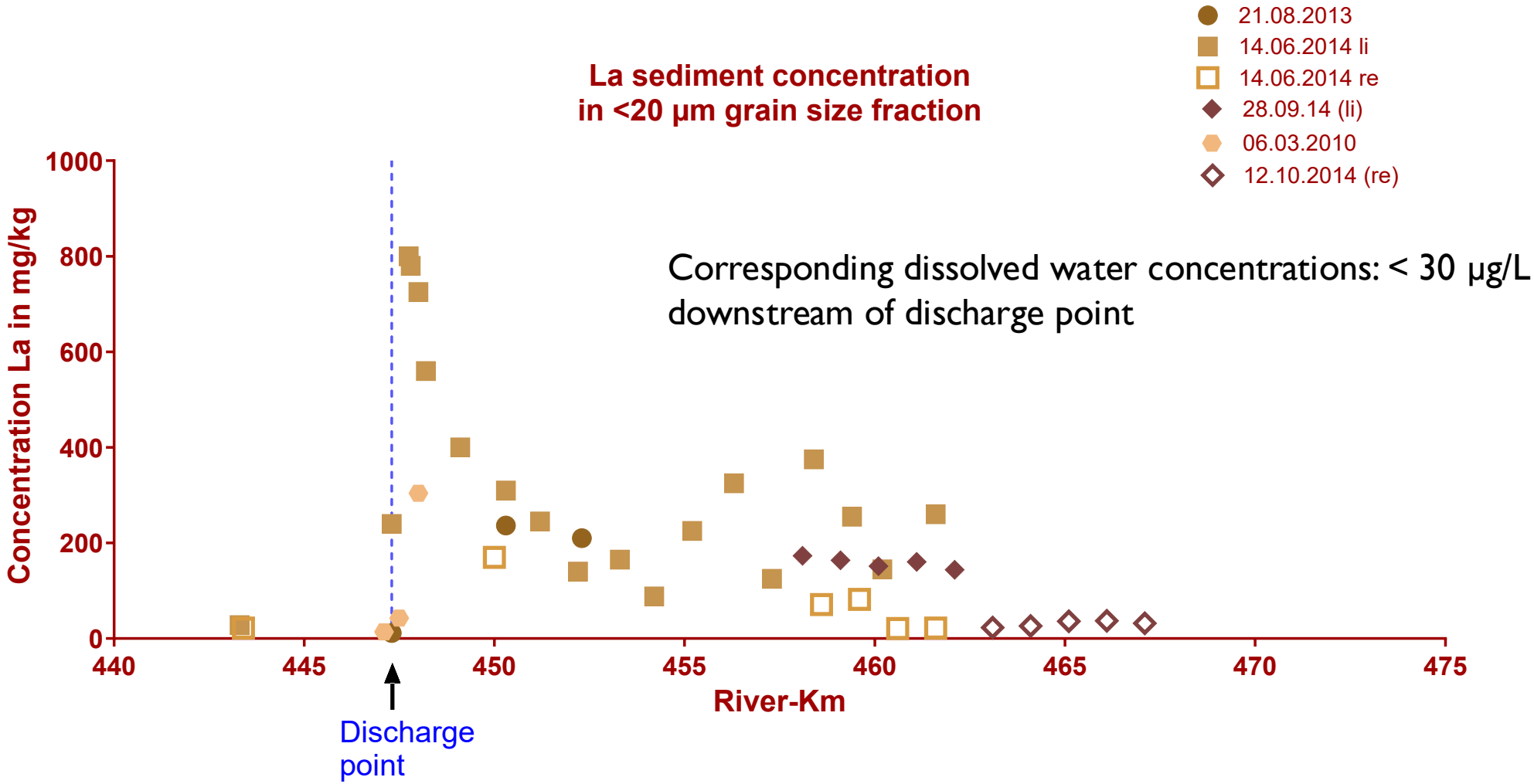
…..

Increasing concern regarding the effects of rising environmental concentrations. (Revel et al. 2024)



Revel, M., van Drimmelen, C.K.E., Weltje, L., Hursthouse, A., Heise, S. (2024) Critical Reviews in Environmental Science and Technology, 1-42.10.1080/10643389.2024.2406992

Industrial emissions of La into the Rhine River



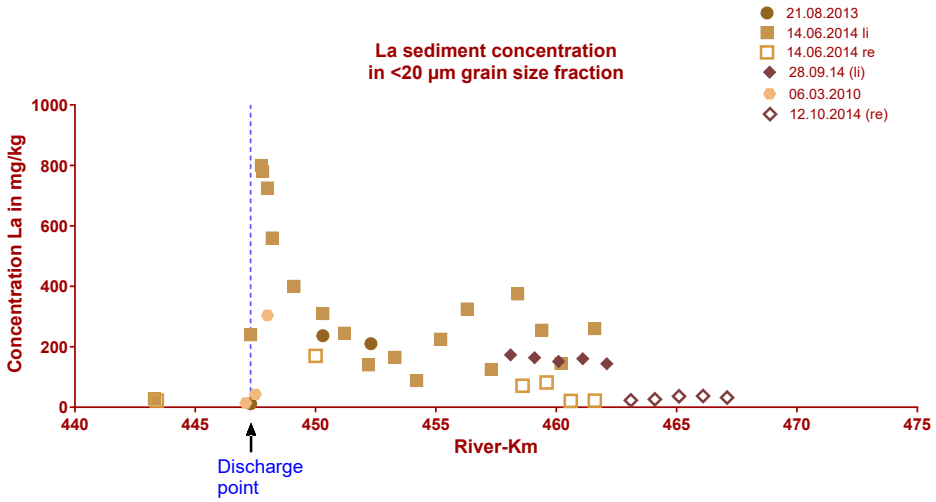
Corresponding dissolved water concentrations: < 30 µg/L
downstream of discharge point

Heise, S., H.Tien, H. Herrmann, S. Berger, J. Nolde and A. Hursthouse (2017), Presentation SEGH conference, Guangzhou, China

Environmental fate of REE in the aquatic systems

[Ln^{3+}] sinks with

- ⬆pH (formation of Ln-hydroxides)
- ⬆organic matter
- ⬆alkalinity (formation of Ln-carbonates)
- ⬆PO_4-concentrations (formation of Ln-phosphates)



Affinity to sediments is high;

Kp-Values (sediment-pore water distribution) is much higher than for other metals.

Most REEs in the aquatic system are found in suspended form or sediment-bound.

Khan, A.M., Bakar, N.K.A., Bakar, A.F.A., Ashraf, M.A. (2017) Environmental Science and Pollution Research 24, 22764-2789. 10.1007/s11356-016-7427-1

Interaction of REE with biological systems

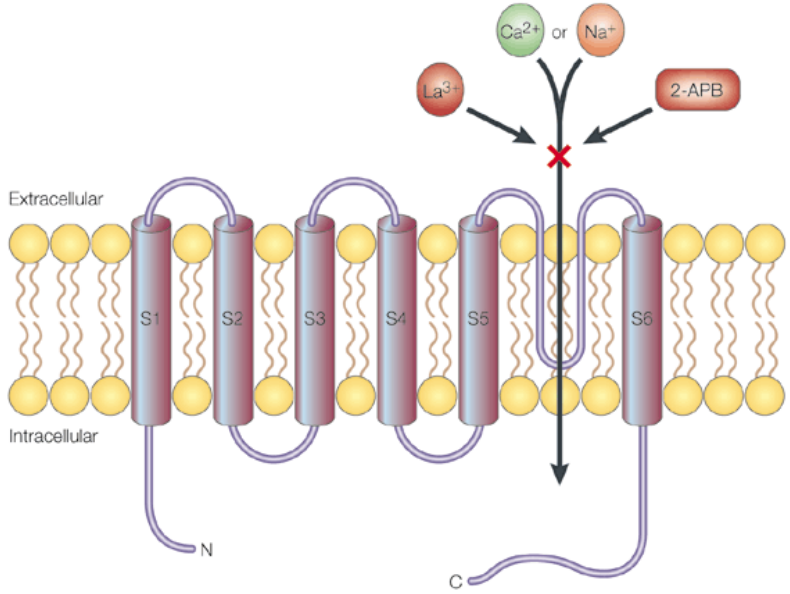
Lanthanum blocks Ca-channels (among others) in the cells

Ca^{2+}: Essential element in all cells — hydrated ionic radius — 0.26 nm (Kiriukhin & Collins 2002)

Ln^{3+} (octahydrates): 0.23 – 0.25 nm (Rudolph & Irmer 2020)

Calcium-Antagonist with a variety of potential physiological consequences (signalling, cell protection, development)

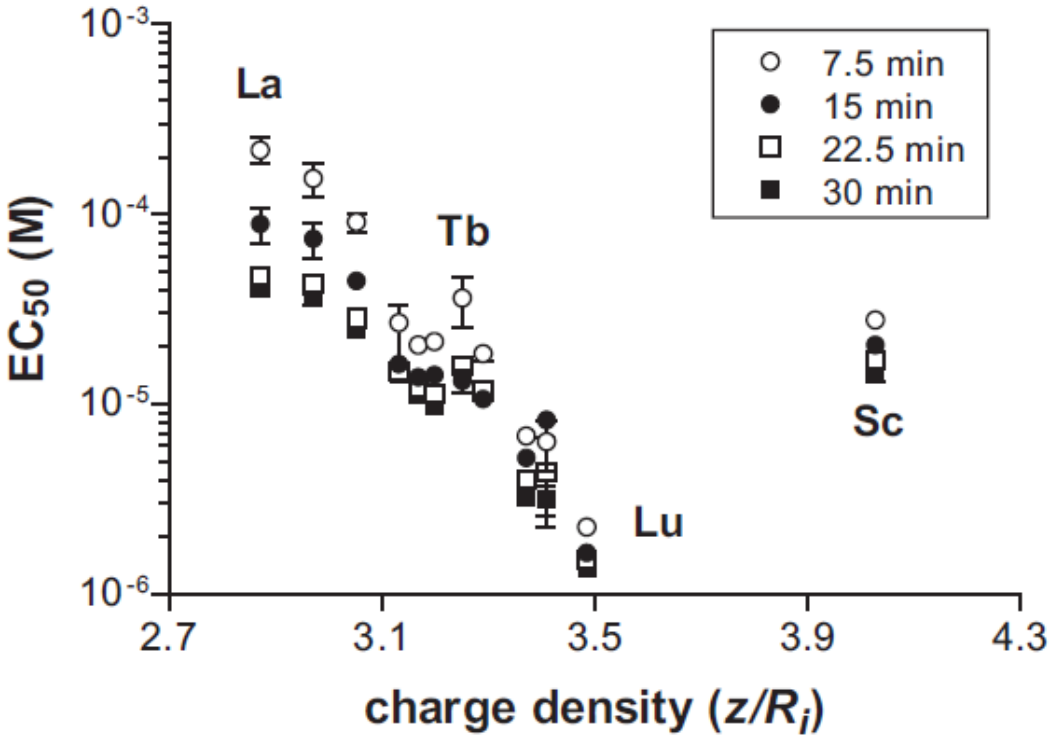
BUT: How toxic is „toxic“?



(Clapham, Runnels et al. 2001) Nature Reviews | Neuroscience

Are they toxic?
Bacteria

EC_{50} values of 11 REE and Sc
when exposed to *Aliivibrio fischeri („Microtox")*



Results from Weltje, 2002:

- Toxicity of Ln comparable to that of Cd, Cu, Pb, Zn
- Toxicity seems to increase with atomic number

Weltje, L. (2002). "Bioavailability of Lanthanides to Freshwater Organisms. Speciation, Accumulation and Toxicity. PhD-Thesis, Delft University.".

Acute daphnia toxicity

Grey: calcium

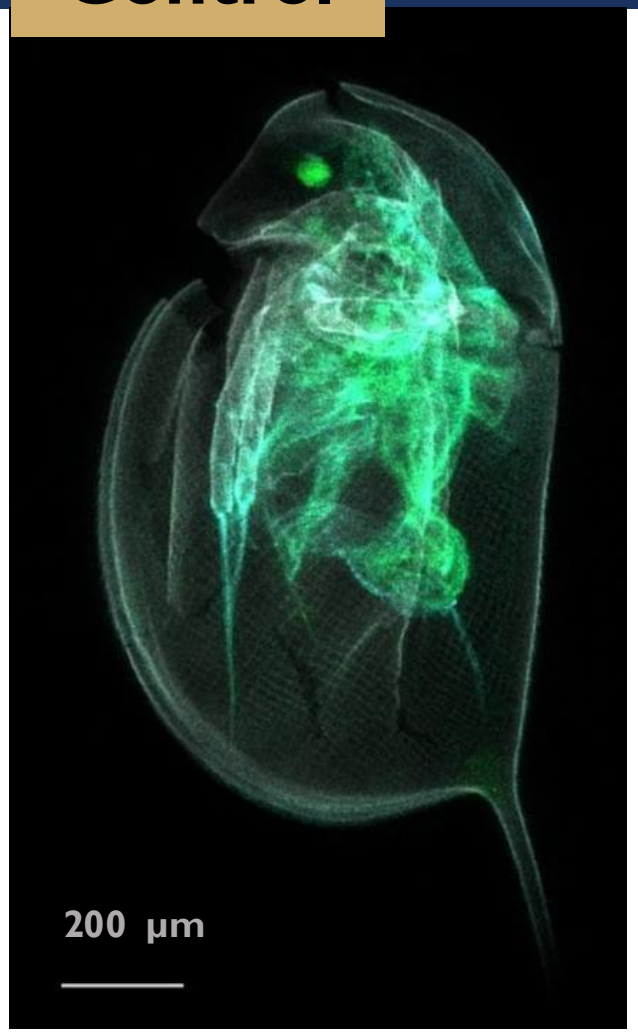
Green: sulfur

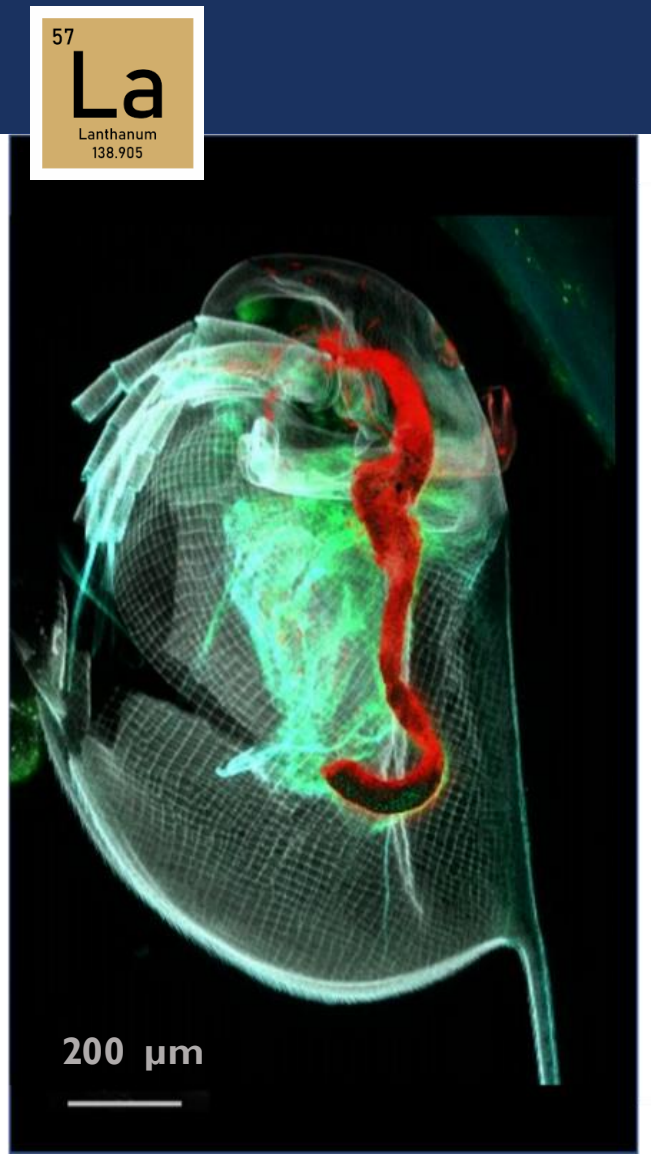
Cyan: phosphorus

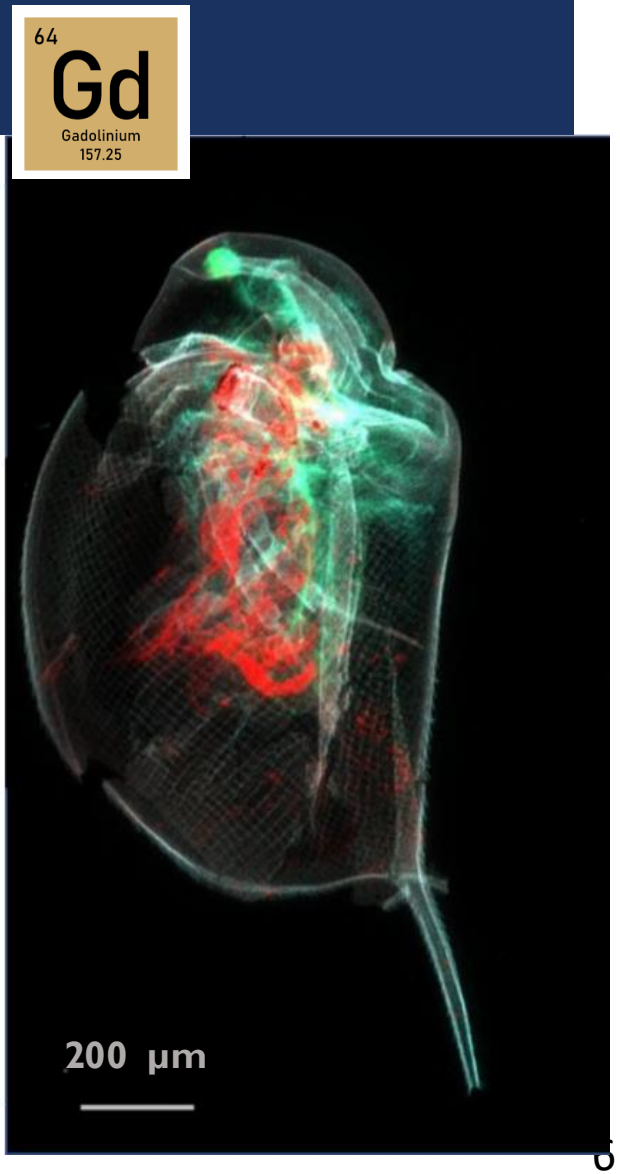
Red: lanthanide

(Revel 2023)

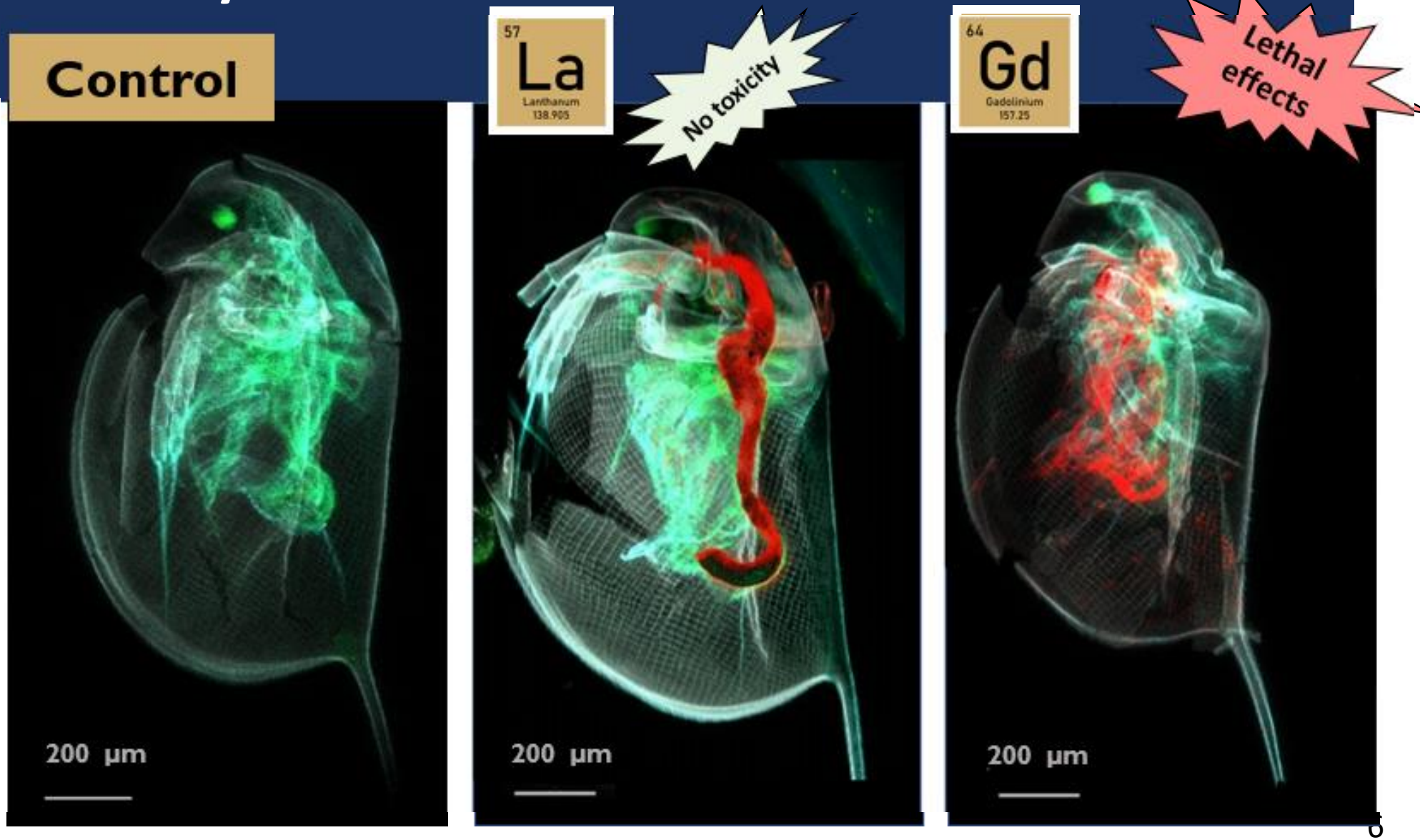
Control





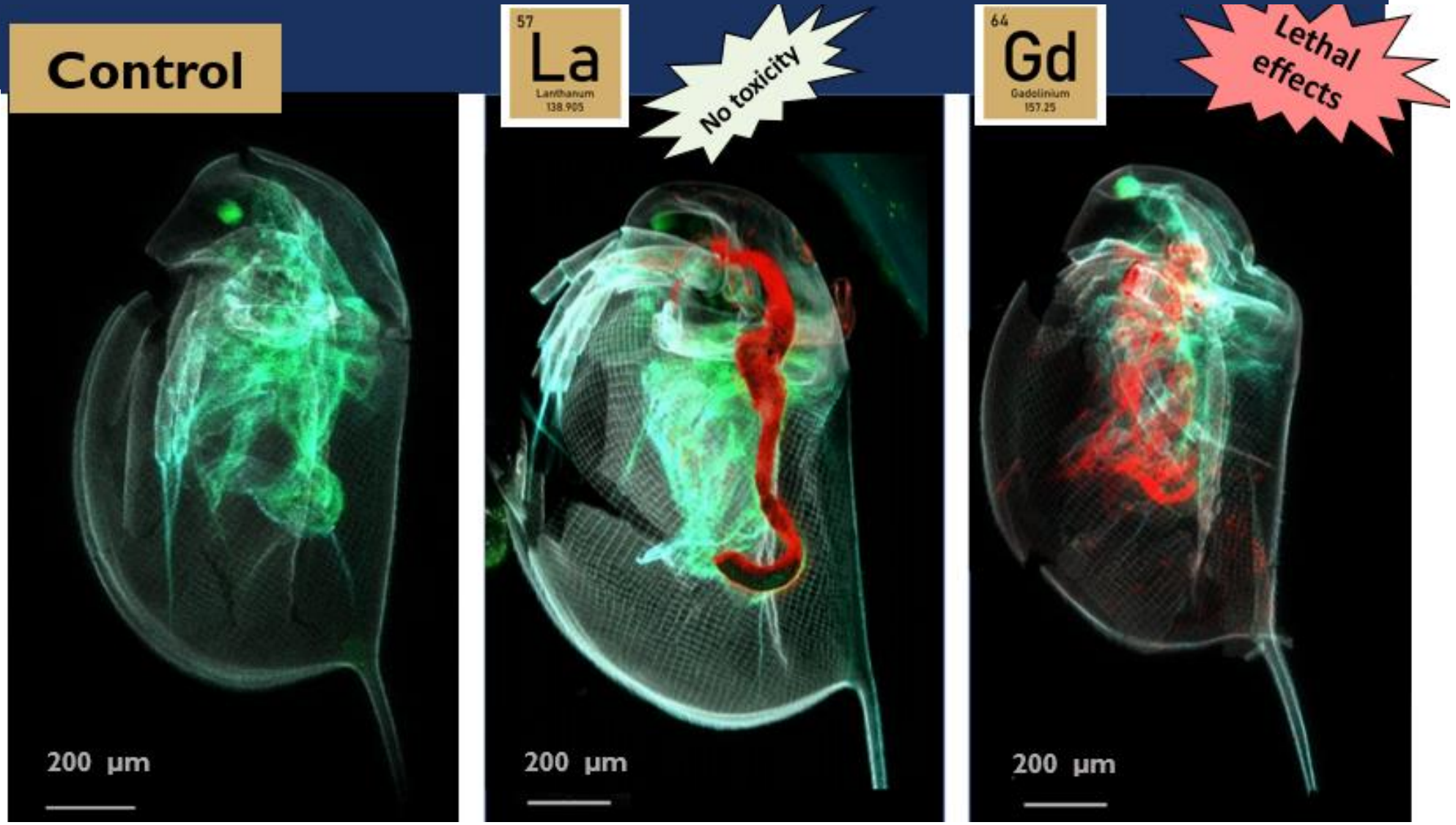


Acute daphnia toxicity

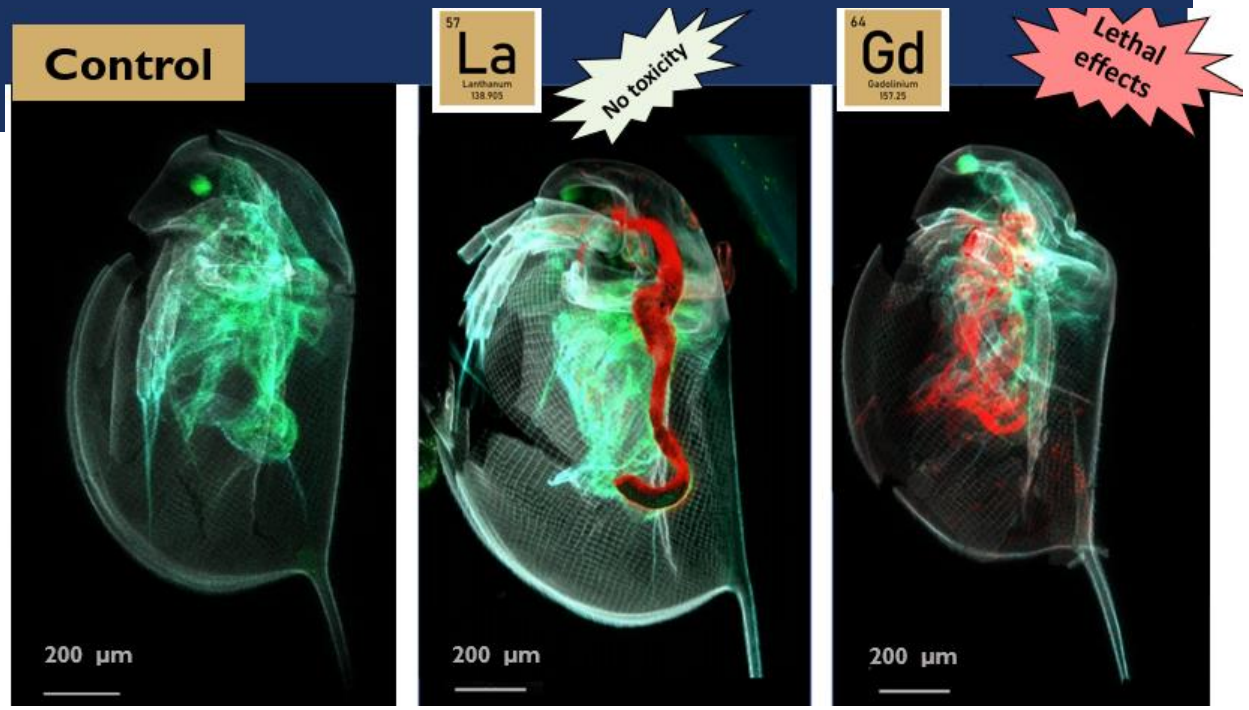


(Revel 2023)

Acute daphnia toxicity



Acute daphnia toxicity



Gd: higher dissolved concentrations than La

→ distributed troughout the tissue, more toxic

⟷ La: probably precipitates, accumulated (and restricted) to GI

Effects on daphnids under acute exposure

IC_{50} (Gd): 13.84 mg/L (11.21 – 23.84 mg/L)

IC_{50} (La): > 30 mg/L

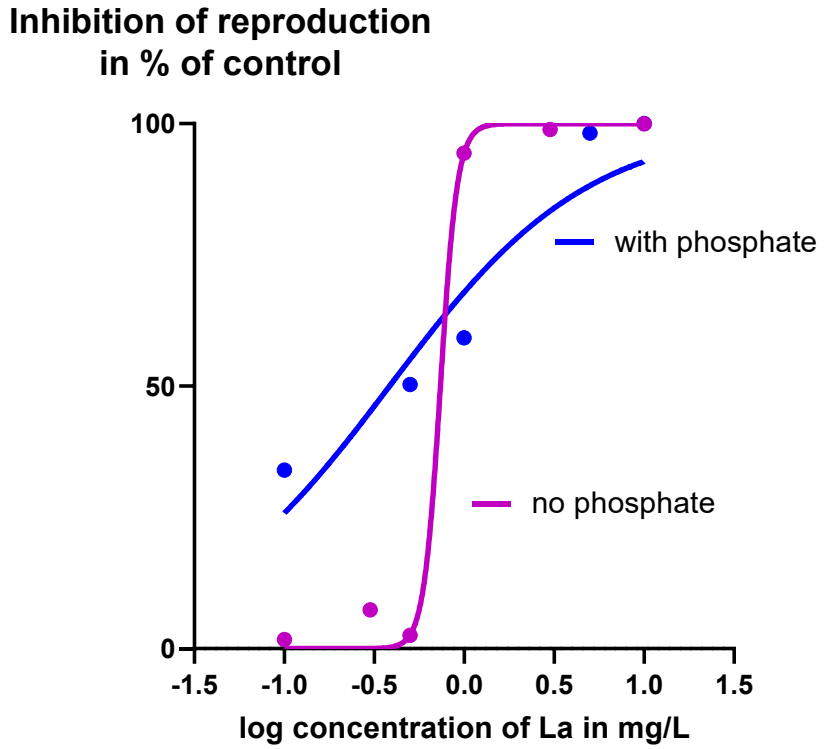
>> than current water concentrations

Toxicity caused by free ions?

Precipitates are not toxic?

Toxicity despite precipitates…

Comparison of dose-response curves for La in nematode bioassay (EC_{50}: 0.38 – 0.6 mg/L) in media with and without phosphate



Data: Ann-Christin Häder 2019; Sebastian Höss 2018

[C]

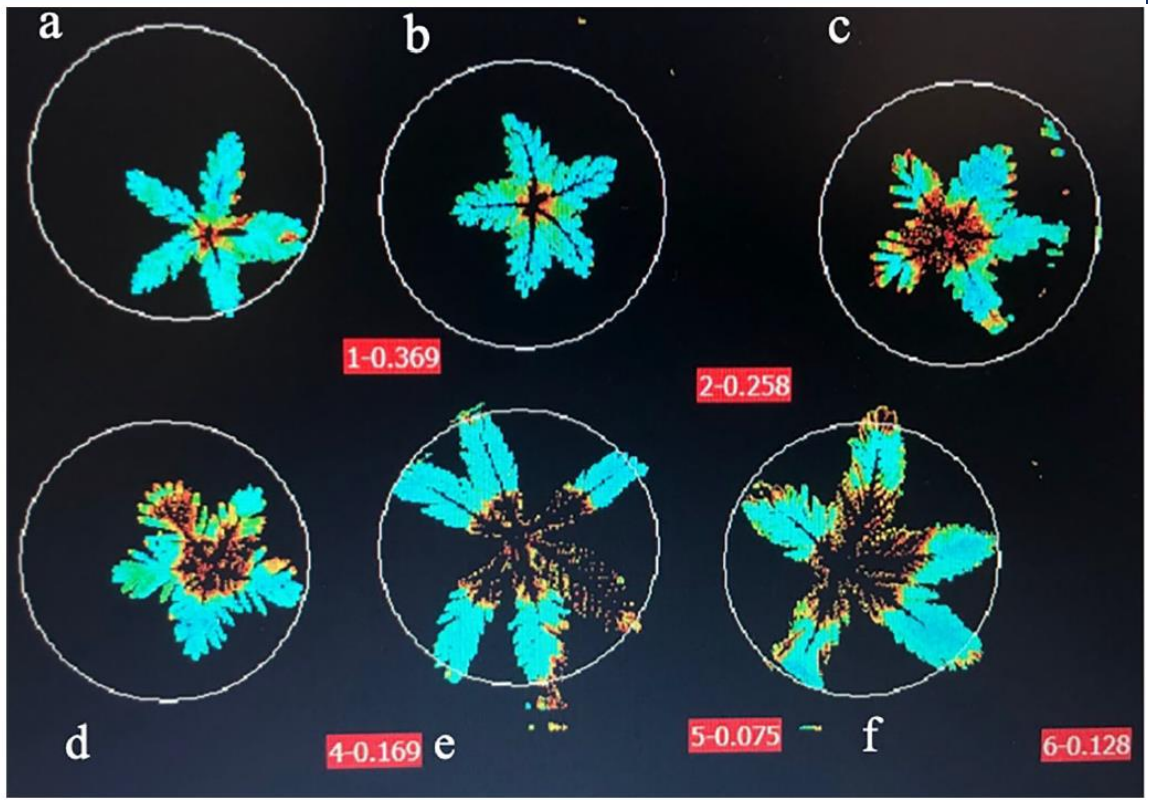
In the presence of phosphate, no La should be available as free ion, but there is a clear dose-response curve, similar EC50.

Uptake of solid phases and remobilization in the gut system?

Sediment toxicity of Gd to a benthic plant

Negative impact of Gd over 10 d

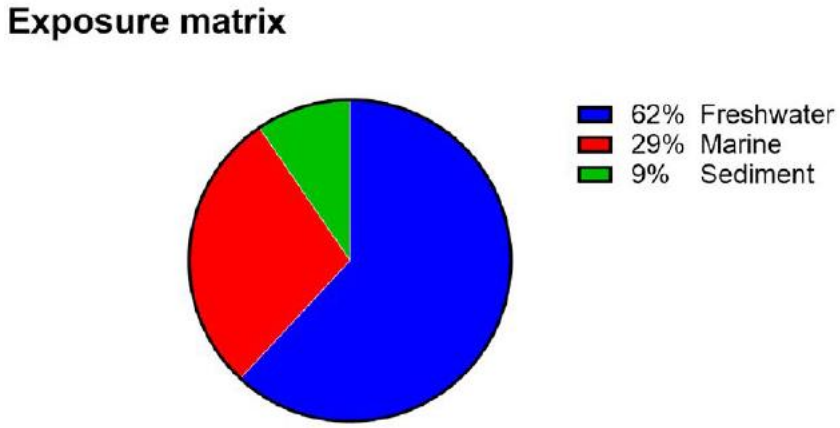
- Growth significantly reduced at 250 mg/kg
- Photosynthetic yield reduced at 500 mg/kg



Chlorosis/Necrosis in *Myriophyllum aquaticum* at different Gd-concentrations in sediments

Summary

- REE have a high affinity to sediments
- With increased use, concentrations in sediments will rise.
- Indications, that precipitates and sediment concentrations will harm aquatic organisms
- The currrent number of ecotoxicity tests for sediment-bound REE is too small to conclude



More data on sediment toxicity are needed, before REE should be assumed to be non-hazardous to aquatic life.