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Rare earths increasingly in the picture

But where do they rank among other metals regarding ecotoxicity and occurrence in the environment?

Nele Deleebeeck, Andreas Fettweis, Laura Lefèvre, Michiel Claessens

SETAC

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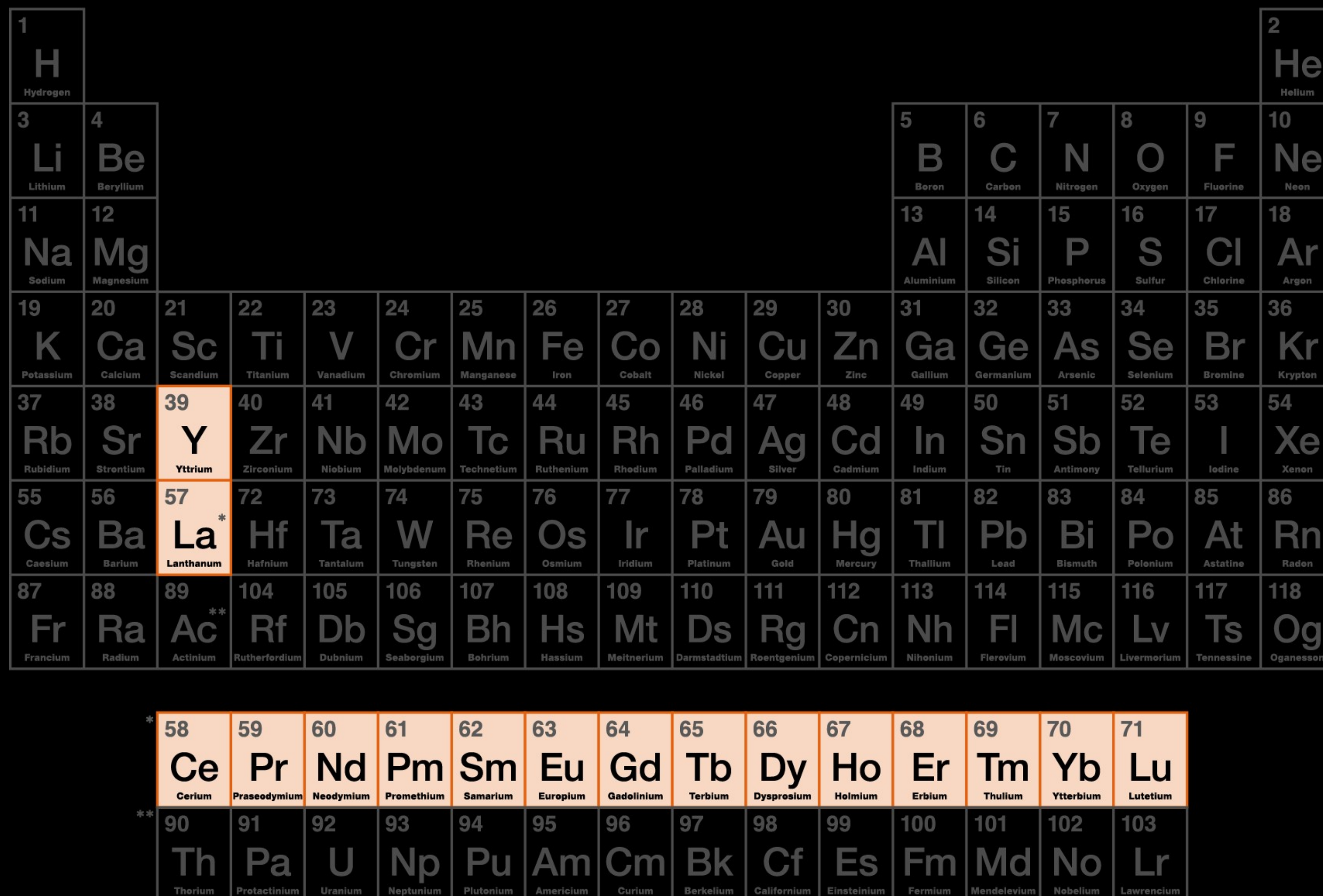


Introduction

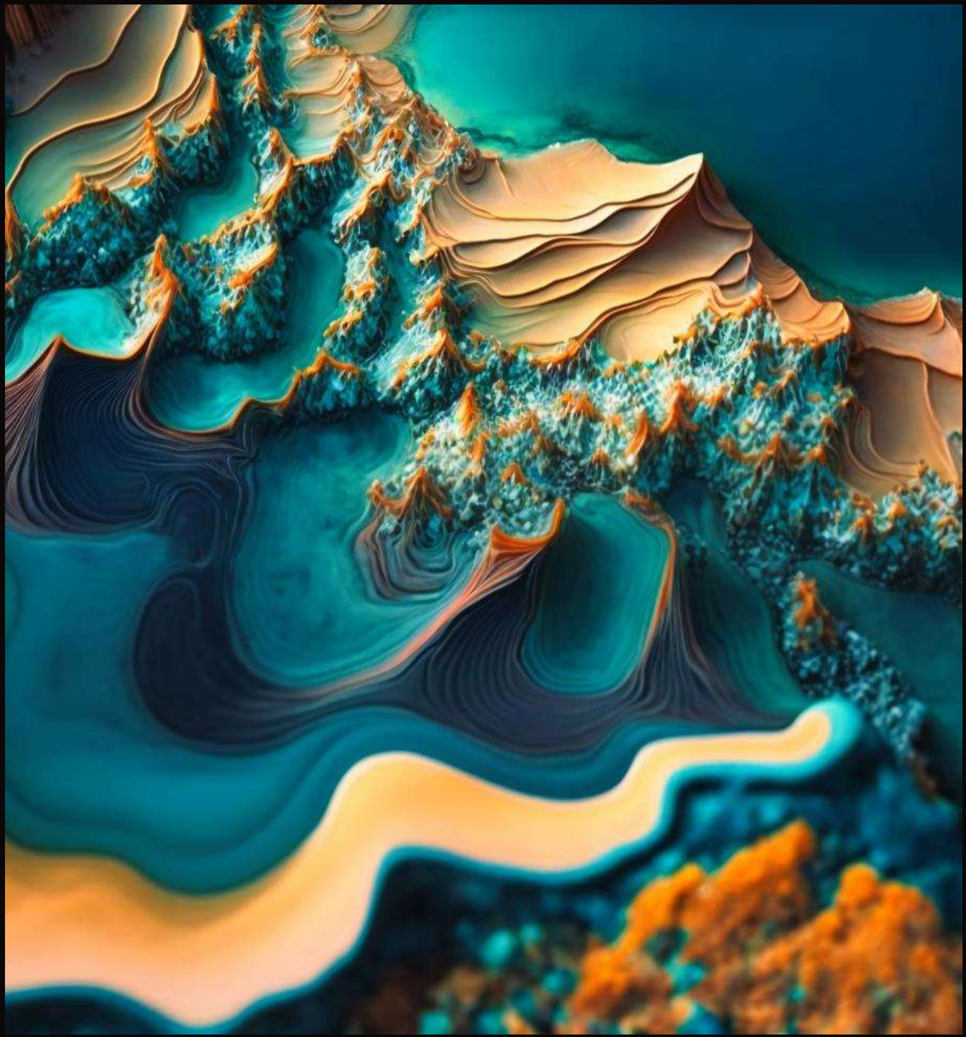
The Rare Earth Consortium was established in May 2008 in view of the EU REACH duties of rare earth manufacturers and importers.

Rare Earth Compounds Reach Consortium | (rare-earth-consortium.eu)

Arcadis is **Consortium manager** for the Rare Earth Consortium and also **provides scientific support** for REACH dossiers.

Under **EU REACH**, dossiers have been submitted for **50 rare earth compounds** covered under the Consortium, for 25 of which Arcadis has provided scientific support.

A lot of data have been generated and evaluated, providing **a substantial knowledge base**



Substances covered by the Rare Earth Consortium

YTTRIUM
(0) metal
(III) oxide
(III) oxalate
(III) fluoride
(III) silicate, Yb-doped
(III) nitrate
(III) chloride

EUROPIUM
(III) oxide

LANTHANUM
(0) metal
(III) carbonate
(III) oxide
(III) hydroxide
(III) fluoride
(III) acetate
(III) nitrate
(III) chloride

GADOLINIUM
(III) oxide
(III) oxalate
(III) nitrate

CERIUM
(0) metal
(III) carbonate
(III) oxalate
(III) fluoride
(III) nitrate
(III) chloride
(IV) oxide
(IV) hydroxide
(IV) nitrate
(IV) ammonium nitrate

TERBIUM
(III,IV) oxide

PRASEODYMIUM
(0) metal
(III) carbonate
(III,IV) oxide
(III) nitrate
(III) chloride

DYSPROSIUM
(III) oxide
(III) nitrate

ERBIUM
(III) oxide

NEODYMIUM
(0) metal
(III) carbonate
(III) oxide
(III) hydroxide
(III) fluoride
(III) nitrate
(III) chloride

YTTERBIUM
(III) oxide

SAMARIUM
(0) metal
(III) oxide
(III) Reaction mass of carbonates of Eu Gd Sm

LUTETIUM
(III) oxide
(III) oxide silicate

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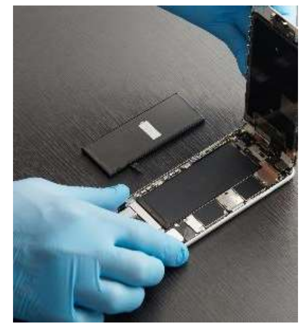
Uses and future needs

Clean and renewable energy
(e.g., permanent magnets used in wind turbine generators)

Hybrid and electric vehicles
(e.g., battery and various other applications)

Catalysts
(industrial, automotive)

Healthcare
(e.g., magnets, imaging, cancer treatment, …)



Electronics and communications

Personal technology
(e.g., rechargeable batteries)

- **Demand can be expected to increase over time**
- **Some are to be considered as Critical Raw Materials**

Aquatic ecotoxicity

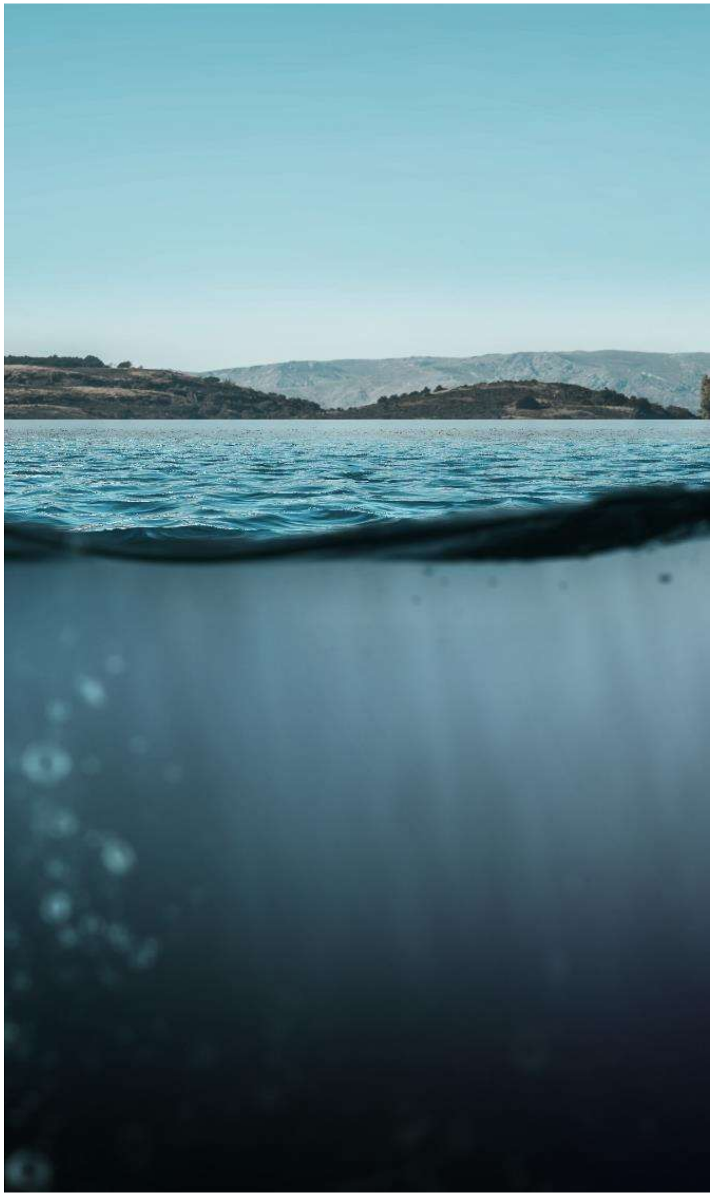
Data availability

(based on currently available data in the REACH dossiers, for algae see further)

1. For most REEs covered by the RE Consortium, reliable **acute data** are available for **fish and aquatic invertebrates**
    - **La, Ce, Nd, Pr, Gd, Dy, Y**

2. Only limited reliable **long-term data** available at time of REACH dossier generation
    - **La, Nd, Dy**

3. General **'rules'** followed **for testing**
    - Semi-static testing
    - Where necessary, testing at low pH to keep stable concentration series (increasing pH results in increasing precipitation of RE hydroxides, carbonates, …)
    - All effect concentrations based on mean-measured dissolved REEs



Aquatic ecotoxicity

- **Acutely, fish** typically **most sensitive**
- **Long-term, much less difference** between fish and aquatic invertebrates, but:
  - Not much data available yet
  - Different test medium composition (literature data) hampers drawing conclusions

Endpoint	Lowest of lowest effect concentrations (all elements)	Highest of lowest effect concentrations (all elements)
Acute fish (LC50)	0.13	0.93
Long-term fish (EC10)	0.035	
Acute invertebrates (EC50)	0.49	6.9
Long-term invertebrates (EC10)	0.0057	0.09

ACR based on data with same test organism in similar test medium → only available for Nd: ACR = ca. 25 for rainbow trout and ca. 110 for *Daphnia magna*

Aquatic ecotoxicity

Algae

- To test **inherent toxicity of rare earths**, a **phosphate source** should be added that is **available to algae but resists complexation by the rare earths**
- Initial REACH testing at CROs: inorganic phosphate used → only indirect effect (**phosphate deprivation**) tested
- Later REACH testing at CROs: canceled as CROs indicated not to be able at that time to replace phosphate source

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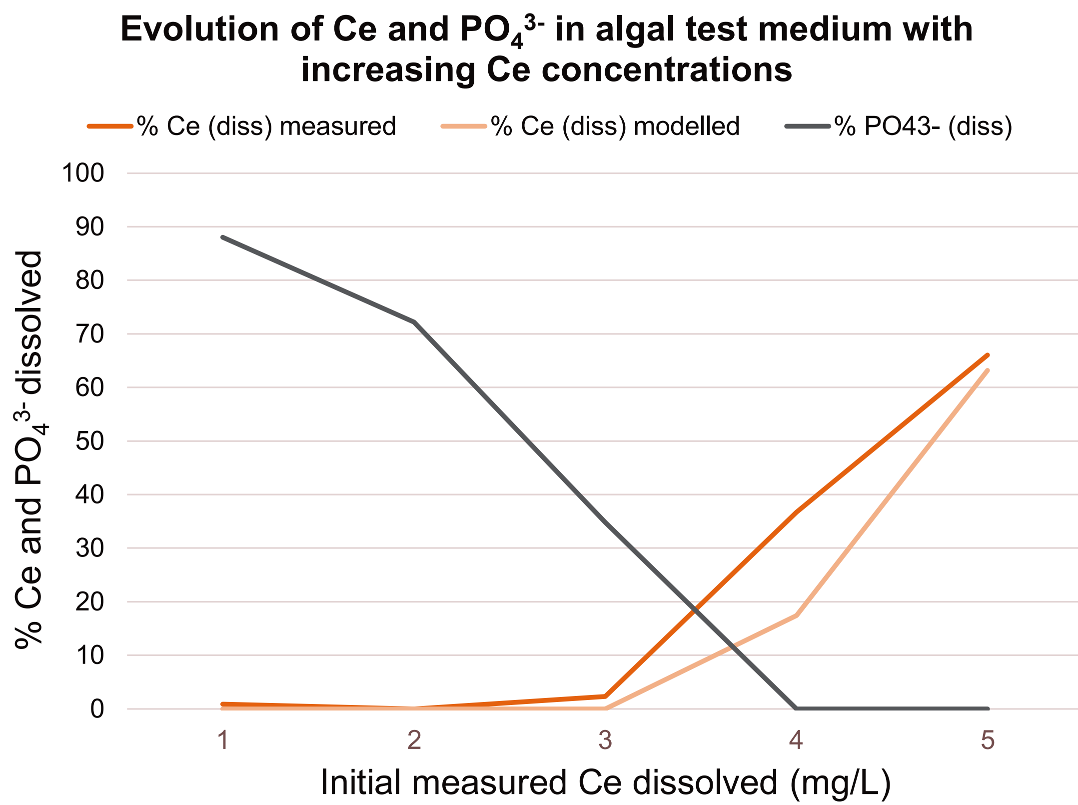

Current PNECaquatic freshwater

- Not enough data to derive PNEC using SSD (species sensitivity distribution) method
- **Assessment factor (AF) method** used
- Algae data (ErC50 and ErC10) excluded (but available data not critical)

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REE	PNECaquatic (µg/L)	AF
Lanthanum	0.6	50
Cerium	0.13	1000
Praseodymium	0.71	1000
Neodymium	3.5	10
Gadolinium	0.43	1000
Dysprosium	0.11	50
Erbium	0.13	1000
Lutetium	2.25	1000
Yttrium	0.2	1000

Margin of improvement for Nd by generation of long-term data with the same test organisms in the same test media was only a factor of 4!!!

Based on acute data, PNEC = 0.87 µg/L

Impact of data from recent / ongoing research projects

- **Acute and long-term data for fish and aquatic invertebrates in line with expectations** based on previously generated / published data
- Increasing insight in **effect of water chemistry** – e.g., DOC, Ca, Na, K, SO4, pH, …

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- Natural Resources Canada
- ECOTREE
- PANORAMA
- REY Elementary

Not all data published / accessible yet

Major difference = algae data

- Use of organically complexed phosphate source to avoid $REPO_4$ precipitation (e.g., β-glycerophosphate, glucose-1-phosphate, cyclic adenosine monophosphate, …)
- **Effect concentrations for 'direct effects' of some studies are unexpectedly low** and might even LOWER PNECs

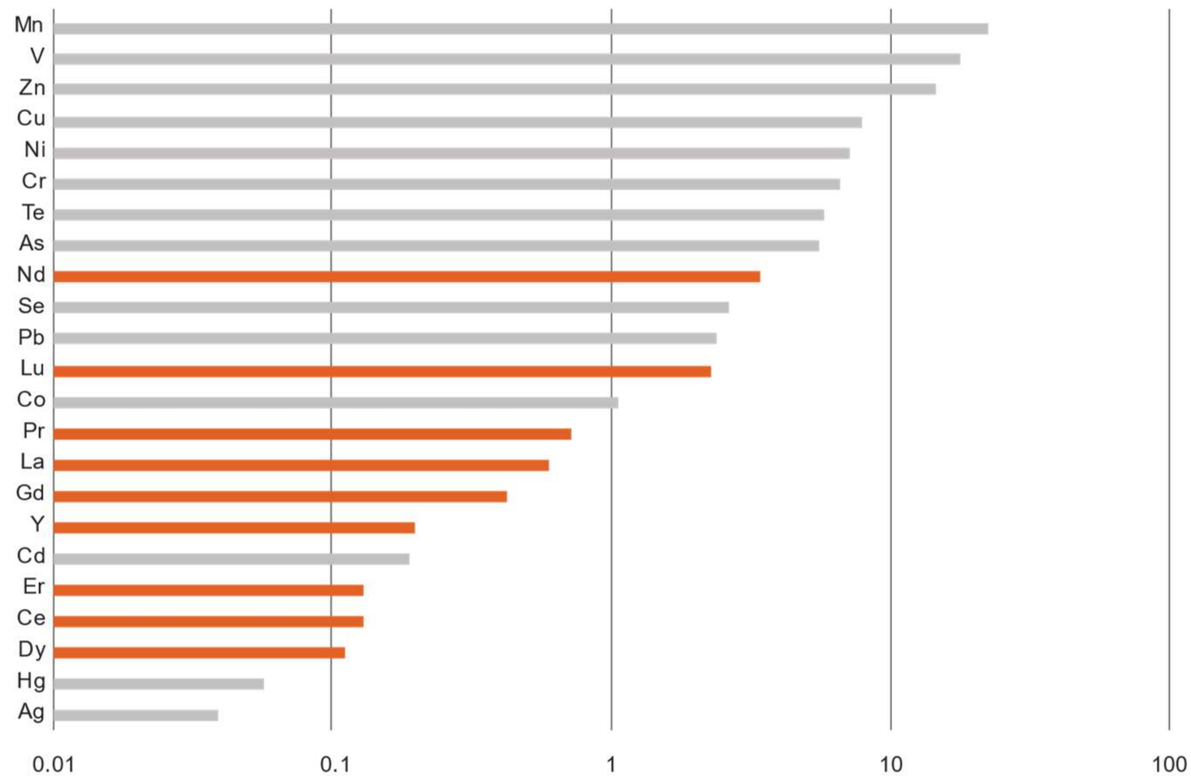
→ **Thorough assessment of results required**

→ Difference explained due to effect of water chemistry? (e.g., soft water testing by NRC)

→ Could the medium adjustment have facilitated RE uptake and toxicity?

PNECaquatic compared to other metals

- **REE PNECs** are **at the lower end**
- Even with **improvement of ecotoxicological dataset**, expected to stay more or less in same position (**factor 4 → max 10 relief expected**)



PNECaquatic, freshwater (µg/L)

PNECaquatic vs measurements in the aquatic environment?

Databases

- **WATERBASE** → No data available
- **FOREGS** (focus on pristine areas) → Data for REEs included

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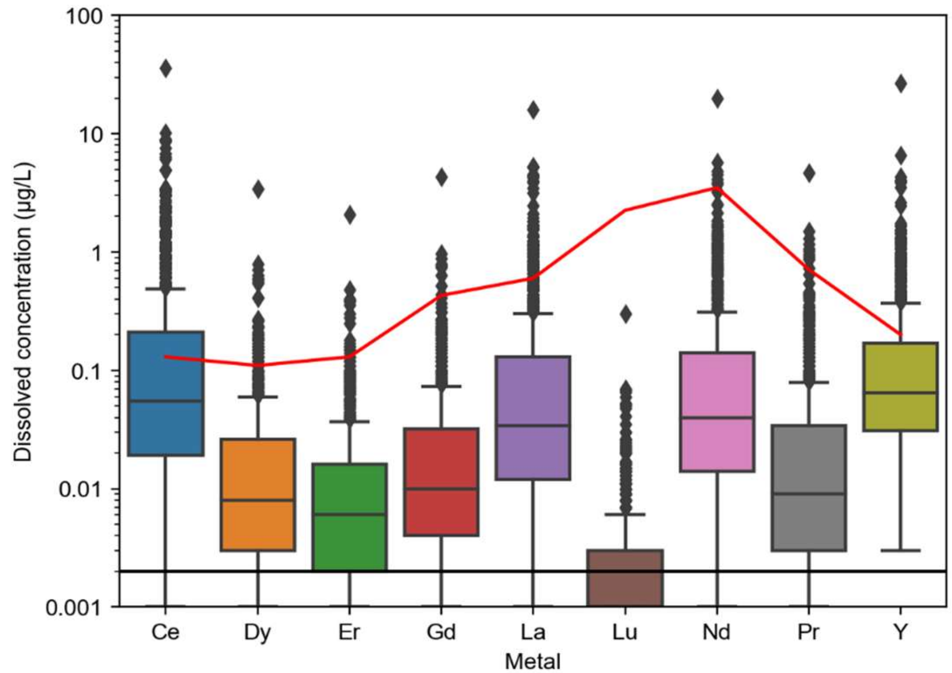
FOREGS – streamwater (n=808)



PNEC vs measurements
For all REEs, PNECaq < max
For Ce and Y, PNEC also < 90th pct

PNECaquatic vs measurements in the aquatic environment?

Literature data

- Screening only
- 5 studies: Kulaksiz and Bau (2007, 2011, 2013), Pignotti et al. (2017), Parent et al. (2018)
- Locations: Germany, Netherlands, France, Italy
- Includes river samples up and downstream from WWTPs
- Measurements not so much different from what is in FOREGS

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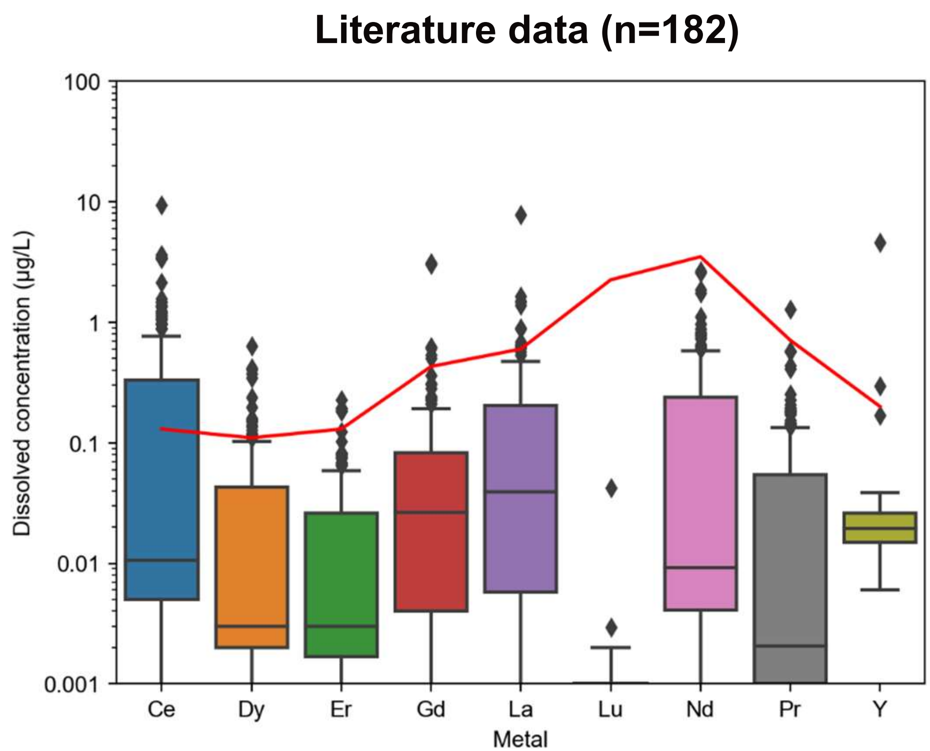


PNEC vs measurements

For most but not all REEs, PNECaq < max

For Ce only, PNEC also < 90^{th} pct

Potential contribution to metal mixture toxicity in the aquatic environment (screening)

Risk quotients (RQ) – mixture assessment based on toxic unit approach

$$RQ_{total} = \sum_{i}^{n} \frac{concentration_i}{PNEC_i}$$

for all metals i considered

Contribution of rare earths to total risk quotient

$$\frac{RQ_{rare\ earths}}{RQ_{other\ metals} + RQ_{rare\ earths}}$$

Rare earths: Y, La, Ce, Pr, Nd, Gd, Dy, Er, Lu (all those for which PNECaquatic available)

Other metals: Ag, As, B, Ba, Cd, Co, Ce, Cu, Ge, Li, Mn, Mo, Ni, Pb, Sb, Se, Te, Ti, V, W, Zn

Various limitations:

- No account taken of added risk approach
- No bioavailability corrections
- Concentration addition is a (worst-case) assumption
- For various metals, including REEs, still margin of improvement on PNECs
- For some REEs, no PNECs available yet

Potential contribution to metal mixture toxicity

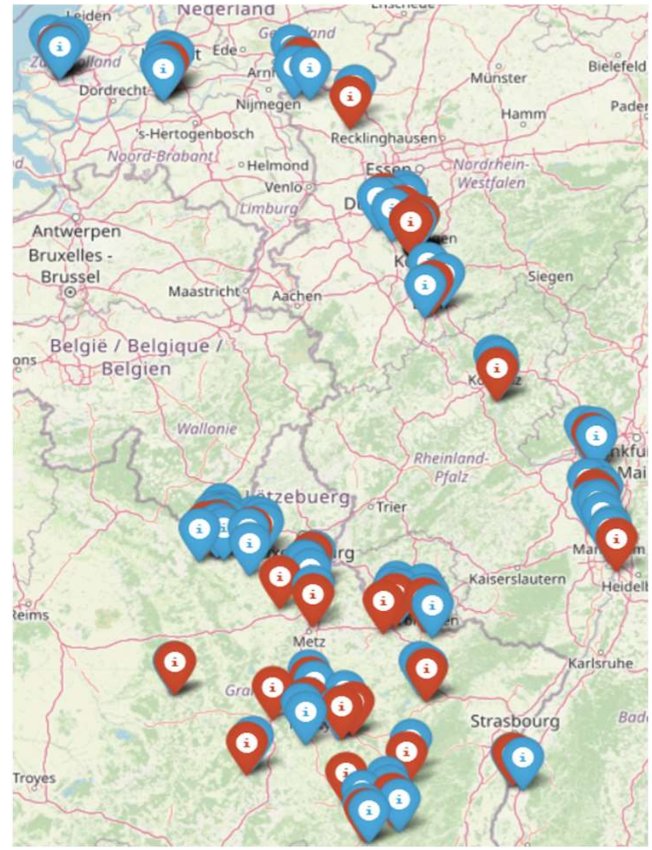
Useful sources need to report measurements for both REEs and other metals!

Literature data
Typically, no joint reporting of measurements for REEs and other metals (or sites with atypically high concentrations for some of the other metals)

WATERBASE
Includes more anthropogenically affected environments (<-> FOREGS)
→ No rare earth measurements

Match sampling locations
WATERBASE monitoring stations (**blue**) → for metal concentrations other than rare earths
Literature data with coordinates (**red**) → rare earth concentrations

- Based on distance and sampling time: 13 matches found
- However, matched WATERBASE stations did not have sufficient data for other metals



Potential contribution to metal mixture toxicity

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Exercise based on FOREGS data

- **MEDIAN contribution of 9 REEs to the total risk quotient** of 30 metals was found to be **ca. 25%** with current PNECs
- Not surprisingly, since this is **1/3 of the total number of metals considered and PNECs are relatively low**

Impact of refinement of hazard assessment?

- Increase of PNECs (only those currently derived using AF of 1000) by:
    - Factor 2 → median contribution ca. 16% ↓
    - Factor 5 → median contribution ca. 10% ↓
    - Factor 10 → median contribution ca. 7% ↓

Conclusion

- REEs are a **large group** of elements, all with **relatively low PNECs**, therefore, the **contribution may be significant**
- However, **a lot is NOT SUFFICIENTLY KNOWN yet**, such as actual bioavailability and effect of water chemistry on ecotoxicity, …

Toxicity to sediment and soil organisms

- Much less data available
- Current PNECs for sediment and soil only derived for Y, La, Ce

REE	PNECsed mg/kg dw	Derivation method	PNECsoil mg/kg dw	Derivation method
Yttrium	36.4	Eq. part.	4.36	Eq. part.
Lanthanum*	13.2	AF 100	0.93	AF 50
Cerium	17.1	Eq. part.	0.451	Eq. part.

*For lanthanum, both AF method and eq. part. were applied, with very similar results!

PNECsed vs measurements in the environment

FOREGS – European stream sediment (mg/kg)

REE	N	Min	Q50	Q90	Max	PNEC
Yttrium	848	1.3	25.7	46.5	426	36.4
Lanthanum	848	1.3	32.5	63.1	553	13.2
Cerium	848	2.2	66.6	135	1080	17.1

PNEC < 90th pct for Y

PNEC < 50th pct for La and Ce

→ Added risk approach to be followed

PNECsoil vs measurements in the environment

GEMAS – European agricultural soil and grassland (mg/kg)

REE	Soil	N	Min	Q10	Q50	Q90	Max	PNEC
Yttrium	Agric.	2108	0.23	2.3	6.7	13	65	4.36
	Grass.	2024	0.23	2.2	6.5	14	77	
Lanthanum	Agric.	2108	1	6.1	14	26	109	0.93
	Grass.	2024	0.93	5.4	14	25	230	
Cerium	Agric.	2108	1.6	11.9	28.4	51.4	265	0.451
	Grass.	2024	1.7	10.5	27.1	48.4	272	

PNEC < 50th pct for Y

PNEC ≤ min for La and Ce

→ Added risk approach to be followed

Conclusions

- Rare earths have **relatively low PNECs.**
- There is **margin of improvement for PNECs**, by generation of more data.
- **PNECaquatic typically > 90^{th} pct measured in EU surface waters** (except for Ce and/or Y)
- PNECsed and PNECsoil are typically < 90^{th} pct measured in EU **sediments and soils → added risk approach** to be considered?
- With current PNECs, **contribution of the REEs to potential mixture toxicity in the aquatic environment** – assuming as a worst case, concentration additivity – **may not be negligible**, especially considering:
  - Current low PNECs
  - Big group of elements compared to total number of metals with known significant hazard in the environment
- **Additional investigations required** on e.g., actual sensitivity of algae, effect of water chemistry on bioavailability in the environment, …

Thank you!

[Rare Earth Compounds Reach Consortium | (rare-earth-consortium.eu)](rare-earth-consortium.eu)

Contact us

Nele Deleebeeck

Senior Environmental Risk Assessor

nele.deleebeeck@arcadis.com