European MARINE BOARD
Advancing Seas & Ocean Science

9th EMB Forum:

Addressing coastal and water resilience at the land-sea interface

2nd April 2025
Institute of Natural Sciences, Brussels
#EMBForum

# Pollution crossing the land-sea interface:

# Pollutants of concern and their pathways


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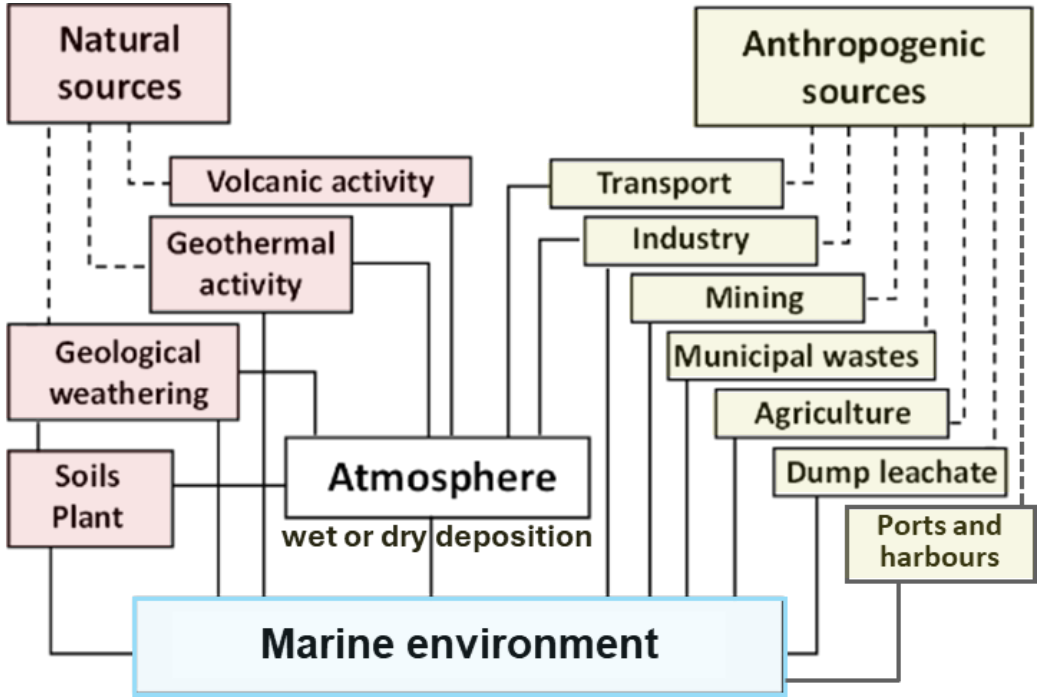
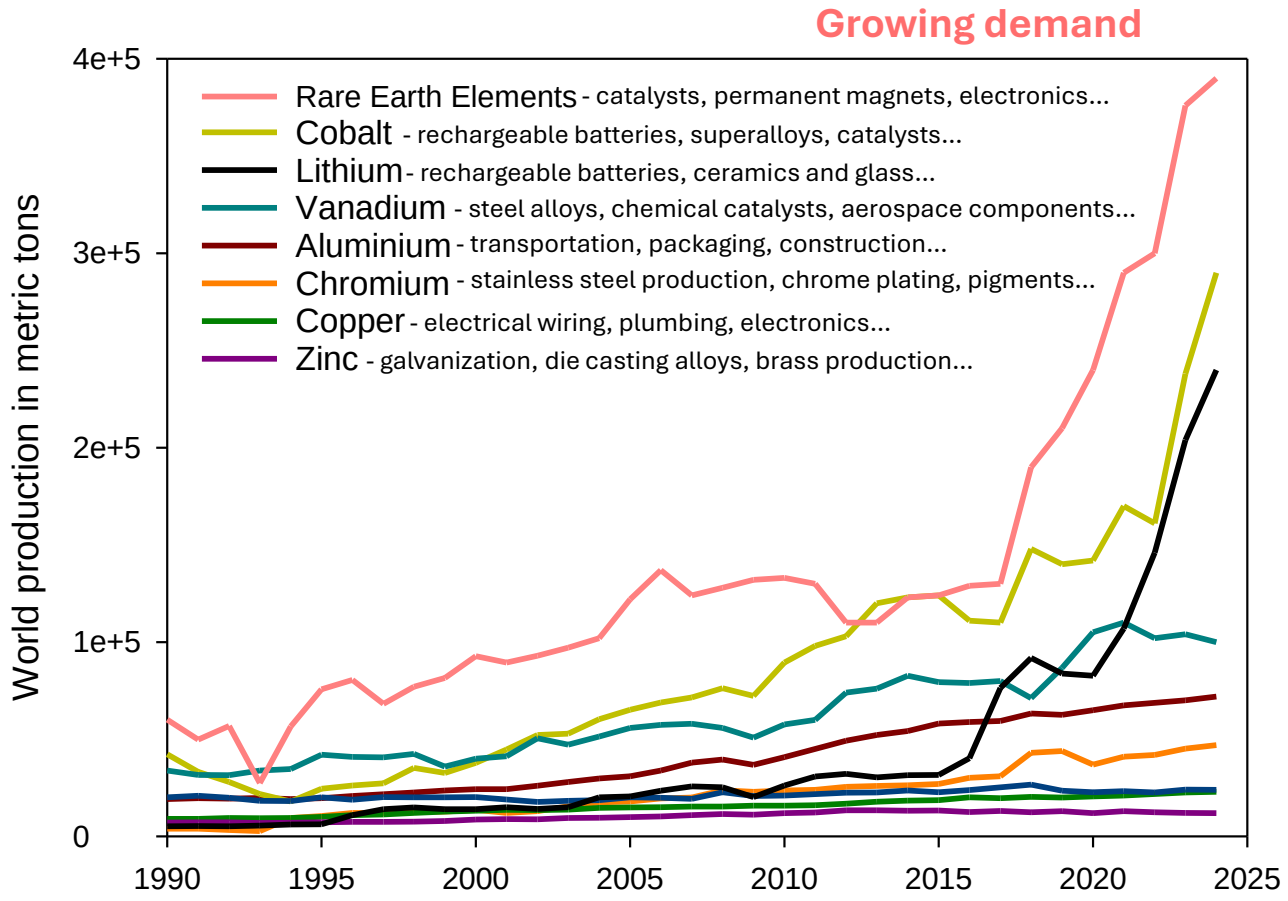
# Trace Metals

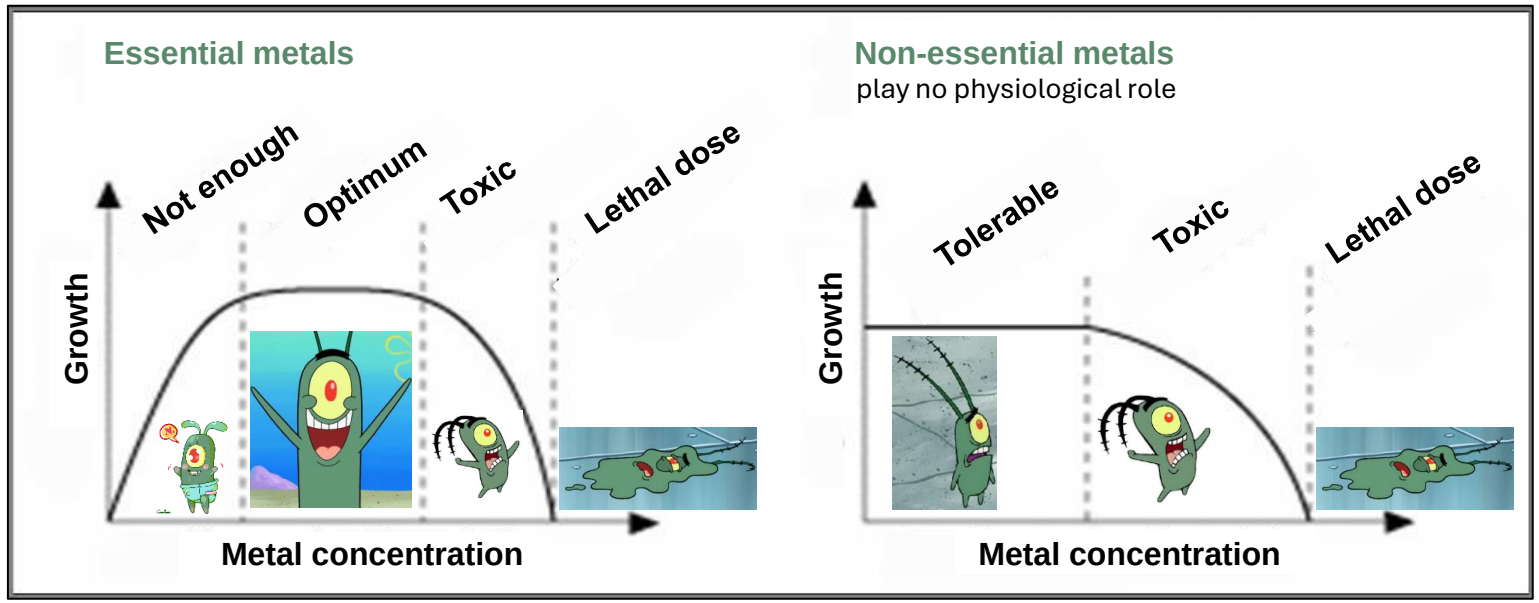
## A Longstanding Pollution with New Dimensions




Data compiled from the Mineral Yearbooks available on US Geological Survey website, www.usgs.gov

# The dose makes the poison

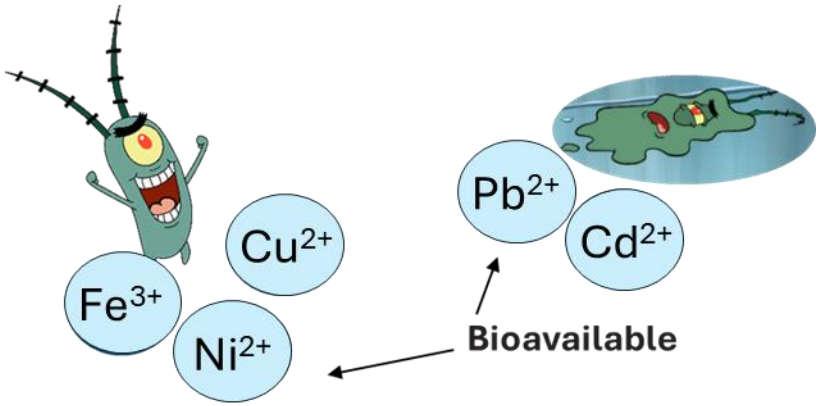


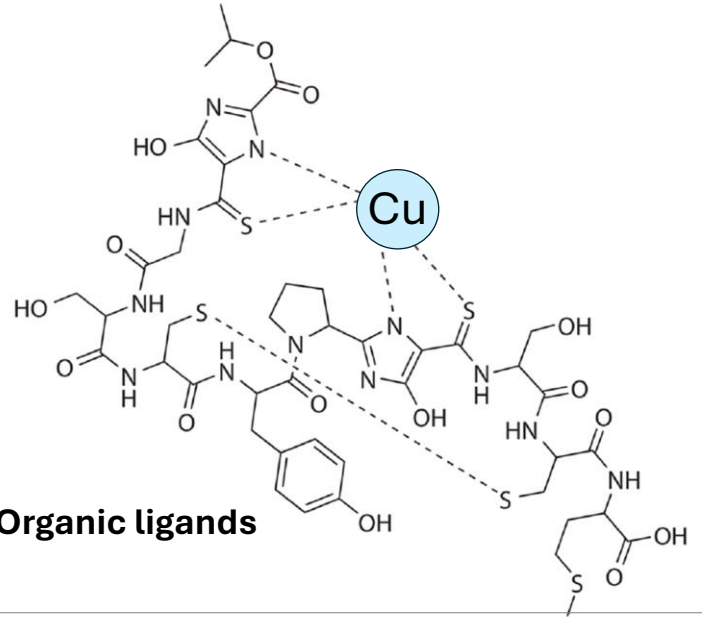

**Total metal concentration** is not sufficient to interpret and predict their biogeochemical behavior

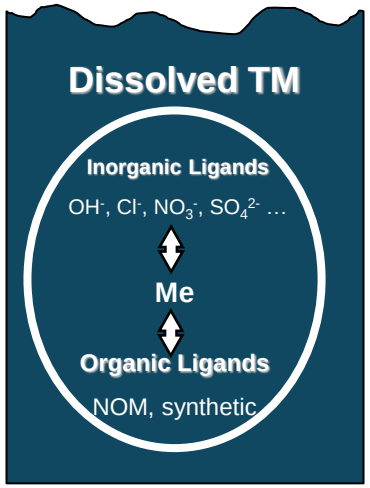
- Bioavailability / toxicity
- Reactivity
- Mobility

Keyword: ***SPECIATION***

Main essential metals for phytoplankton:
**Fe ~ Zn > Mn ~ Ni ~ Cu >> Co ~ Cd**



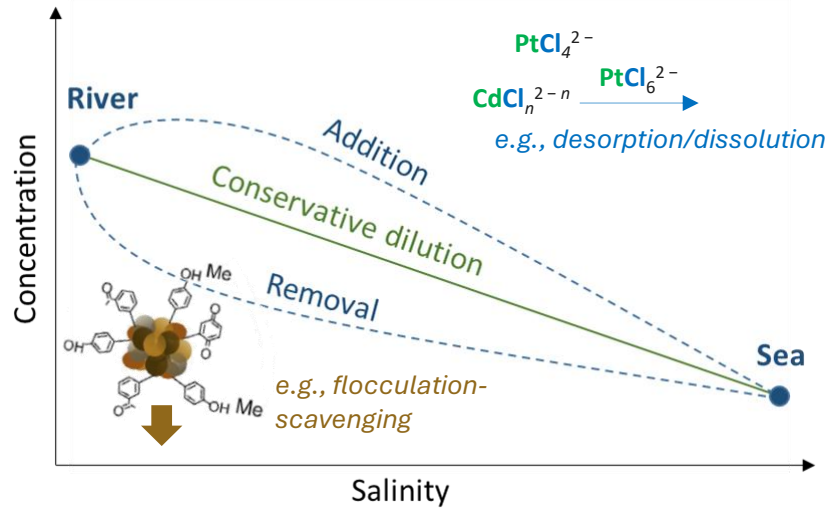



# Complex dynamics in transitional waters

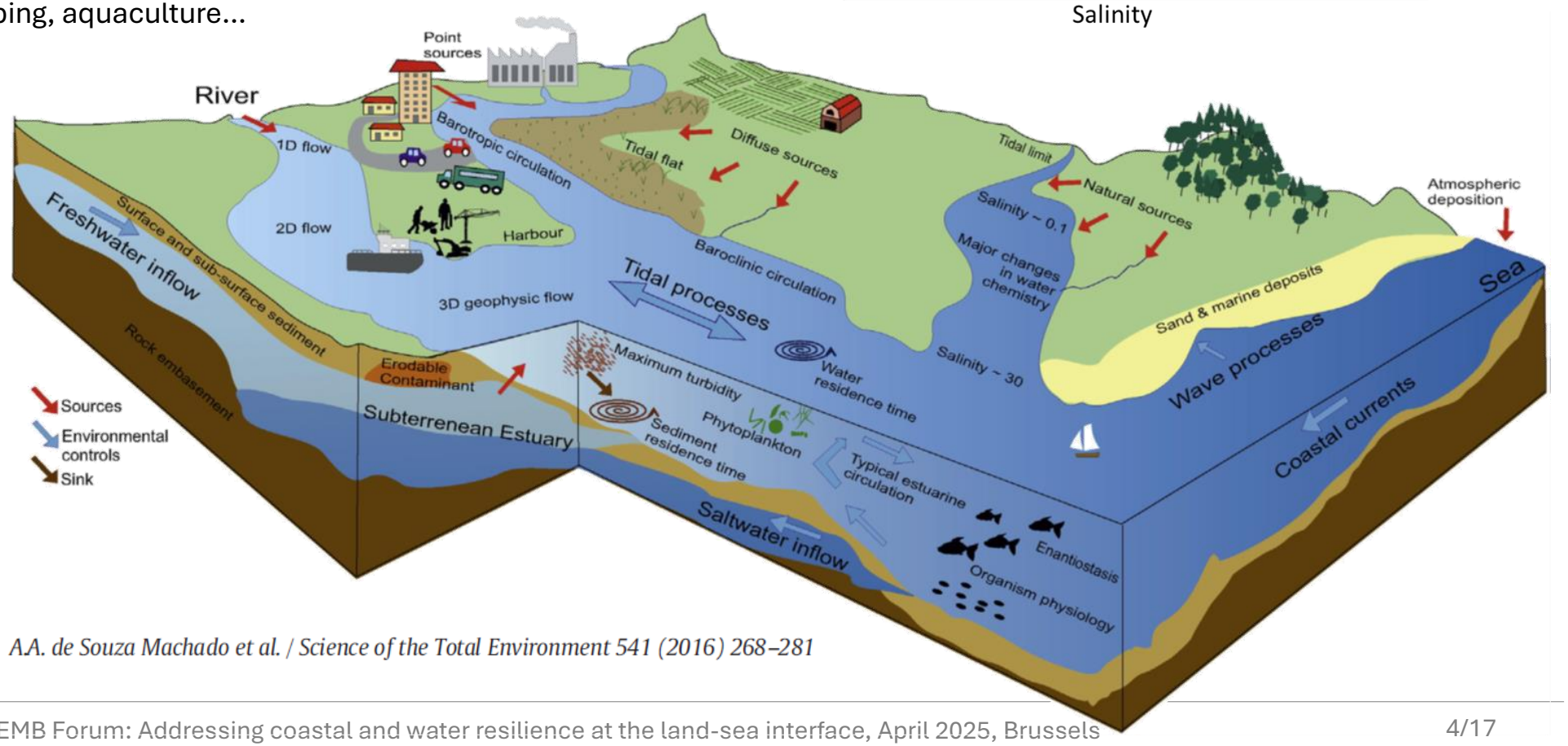
**Trace metals controlled by many interactive factors:**

- **Chemical composition** - ionic strength, pH, major/minor elements
- Abundance of **adsorbing surfaces**
- **Organic ligands** (quantity and composition)
- **Hydrodynamic conditions** - water circulation, turbulent mixing, tidal processes, waves…
- Density, turbidity
- **Biological activity** - microbial processes, eutrophication, grazing…
- **Urban activities** - dredging, shipping, aquaculture…




**Processes:**

- Precipitation/dissolution
- Adsorption/desorption
- Coagulation, flocculation
- Sedimentation/resuspension
- Biological uptake
- Transport/exchange between compartments



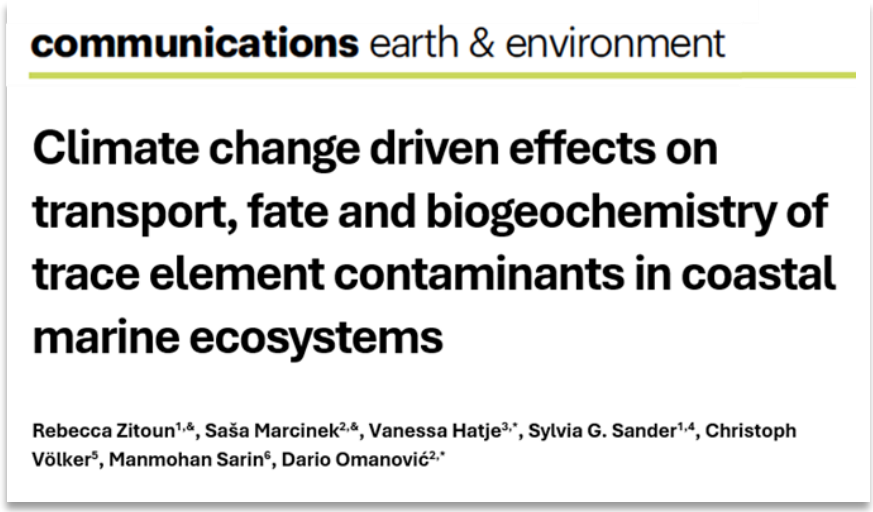

*A.A. de Souza Machado et al. / Science of the Total Environment 541 (2016) 268–281*

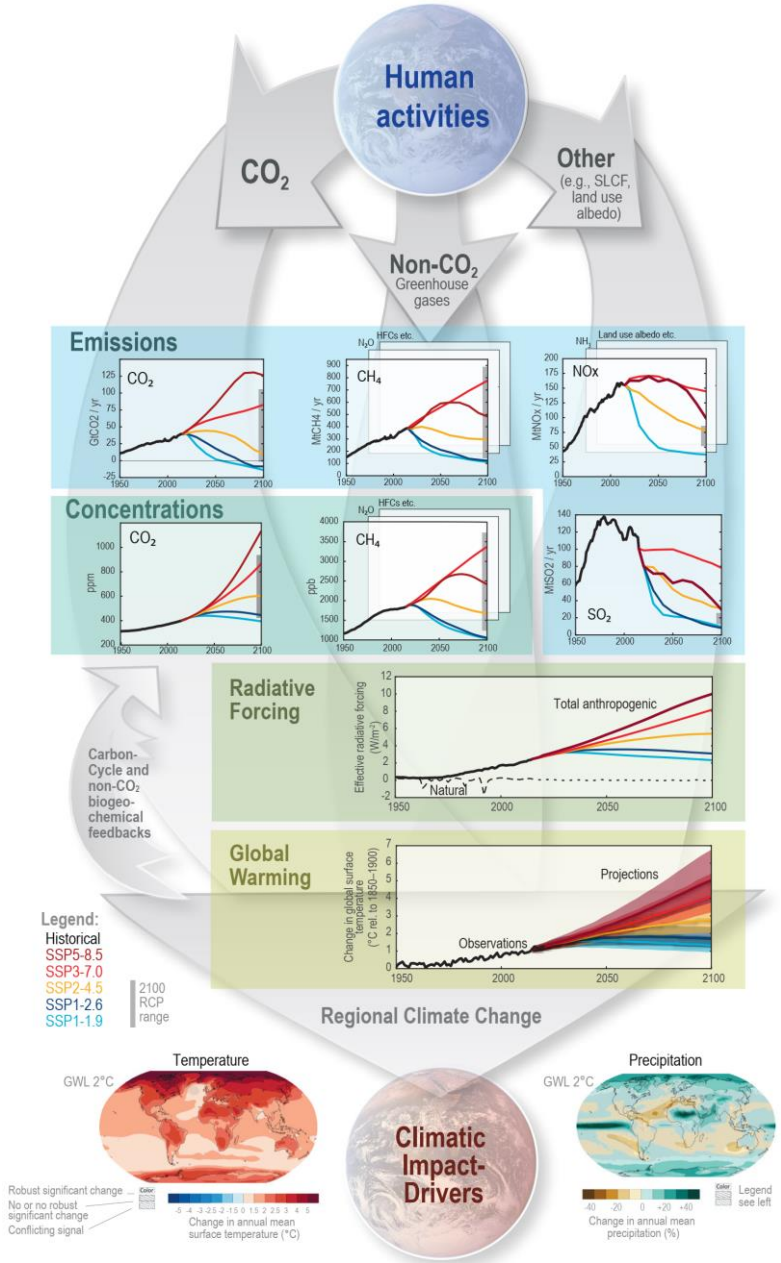
# Trace Metal Dilemma: Persistent Pollutants in a Changing Environment

GESAMP
Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection

IAEA UNESCO IOC WMO IMO UNEP

**July 2021 WG 45**
**Climate Change and Greenhouse Gas Related Impacts on Contaminants in the Ocean**


IPCC AR6, 2021, WG1

# Climate change drivers

(primary and secondary)

- Ocean warming
- Ocean acidification
- Changes in hydrological cycle
- Extreme weather events
- Ice melting
- Sea-level rise
- UV radiation
- Salinity changes
- Deoxygenation
- Ocean circulation/mixing changes
- Combination of stressors

***Natural causes***

- *Volcanic eruption*
- *Ocean currents*
- *Earth orbital changes*
- *Solar variation*

***Human causes***

- *Greenhouse gases*
- *Burning of fossil fuels*
- *Deforestation*
- *Coal mining*

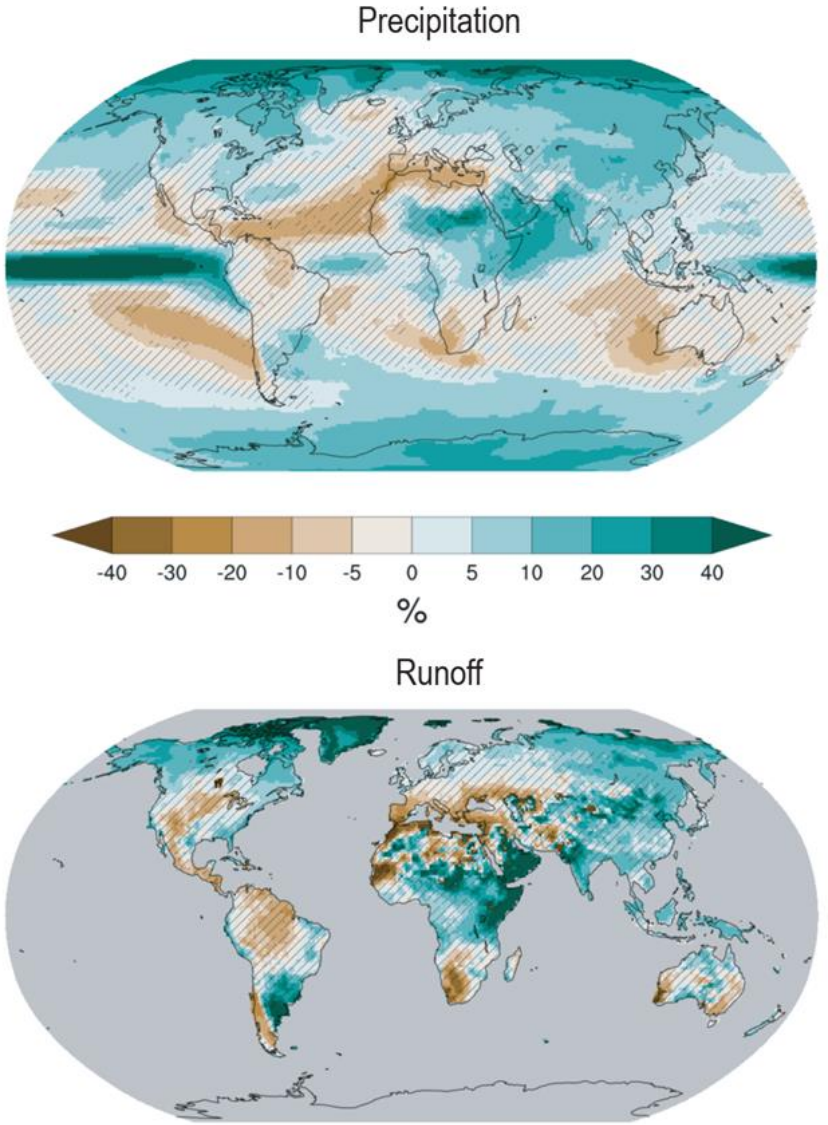
1. Impacts on **sources and transport pathways** of trace metals to the sea
2. Changes in trace metal **biogeochemical cycles** in the sea
3. Impacts on **biological response/sensitivity** to trace metal stressors

**Predictions by the end of the century:**

- **Ocean acidification** → decrease in the surface ocean pH by **≈ 0.3 - 0.5** units
- **Ocean warming** → increase in avg sea-surface temperature by **0.7 - 2.7 °C**
- **Global precipitation average** → increase by **2%**
- **Sea-level rise** by **0.3 - 1.0 m**

# 1. Impacts on trace metals **sources**

- **Hydrological and aeolian transport pathways**
  - Precipitation and dust input
  - Riverine discharge and runoff
  - Submarine groundwater discharge (SGD)




**Long-term water cycle variables changes for SSP2-4.5 (2081–2100 vs 1995–2014)**

**IPCC AR6, 2021, WG1**

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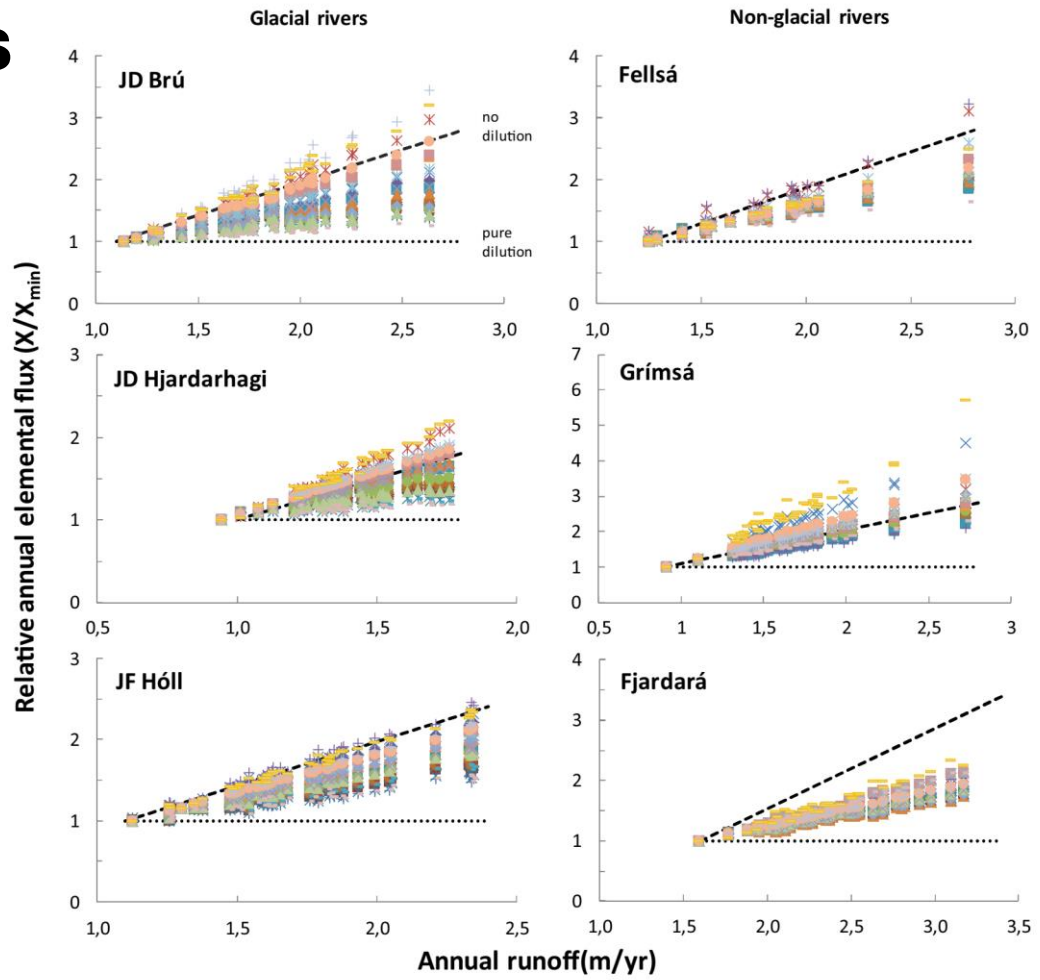
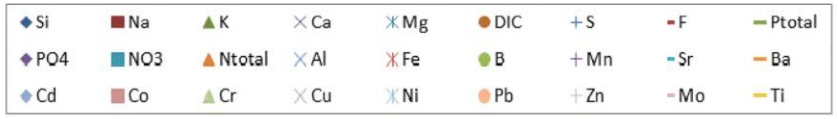
**River catchments in Eastern Iceland**




**Period 1961 - 2004**

Trace metal flux increase
**6-18% per °C**




Eiriksdottir et al., 2015, *Geochimica et Cosmochimica Acta*

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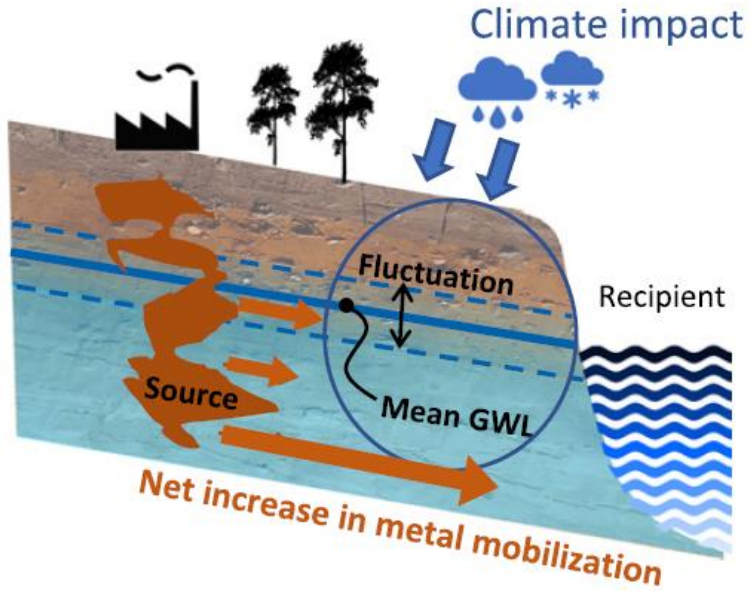
A




Jarsjö et al., 2020, *Science of the Total Environment*

Model projections of changes in **As** and **Pb** mobilization in response to possible future **increase in groundwater level** and fluctuation **amplitudes**

**2-10x** increase in mass flows per **0.2 m** SGD increase

Moderate projections for Northern Europe in next 20 years

B

**Decrease in SGD flux** + **sea-level rise** (+) temperature rise = **seawater intrusions** into coastal aquifers = **change in chemistry** (salinity, pH, oxygen levels)

***Implications***: *e.g., desorption from Fe-oxyhydroxides (e.g., **As**, **Pb**) or increased **Hg** methylation*

# 1. Impacts on trace metals **sources**

- **Hydrological and aeolian transport pathways**
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  - Submarine groundwater discharge (SGD)
- **Sediments and coastal erosion**

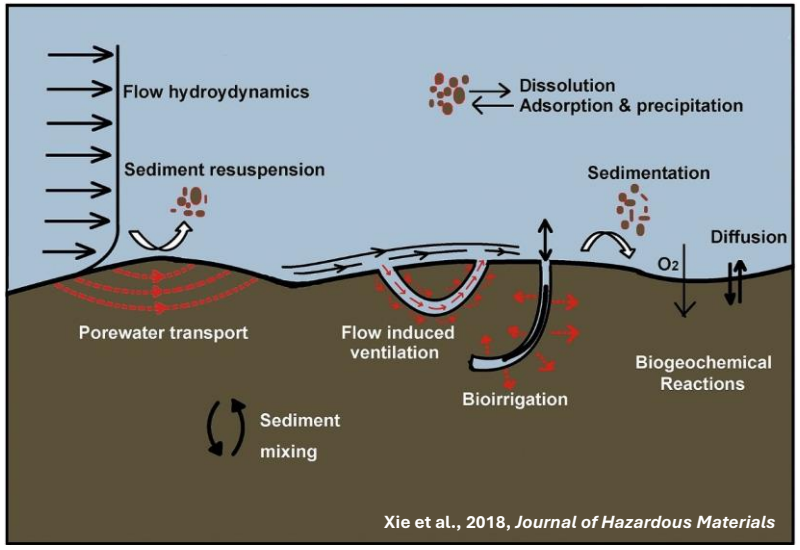
➢ **Sea-level rise**
➢ **Extreme weather events:**
Floods, Droughts, (meteo)tsunamis, Hurricanes…

⇩

- Increase the diffusive flux of contaminants
- Erode sediments (landfills, mining ponds…)
- Transport/redistribution of contaminants

**Controls on trace metal mobility in sediments:**

- Sediment **redox potential**
- **pH** changes
- **Dissolved organic matter** content
- **Fe/Mn hydroxides** reductive dissolution
- **Sulphate reduction**

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- **Hydrological and aeolian transport pathways**
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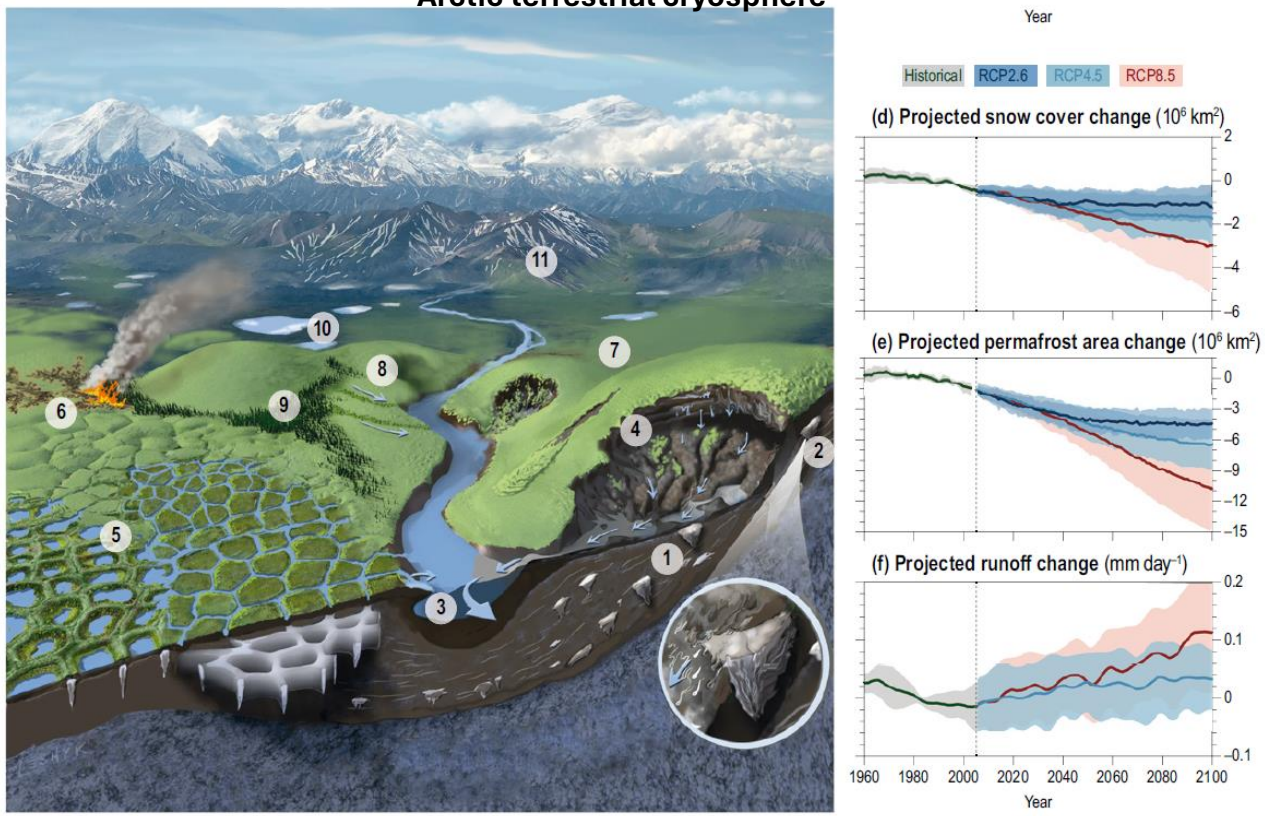
- **Sediments and coastal erosion**
- **Cryosphere under climate change**
  - Glacier/ice melting
  - Permafrost melting
  - Glacier erosion
  - Sea-ice and ocean currents transport

„Permafrost soils store **nearly twice as much Hg** as all other soils, the ocean, and the atmosphere combined, and this Hg is **vulnerable to release as permafrost thaws** over the next century."

Schuster et al., 2018, *Geophysical Research Letters*

**Arctic terrestrial cryosphere**




IPCC Special Report on the Ocean and Cryosphere in a Changing Climate, 2019

„Up to **65% of the Arctic's near-surface permafrost** may be lost by 2100, releasing known and unknown hazards into the global environment"

Miner et al., 2021, *Nature Climate Change*

# 2. Impacts on trace metal **biogeochemical cycles**

- Reactivity
- Transport
- Bioavailability!

Keyword: ***SPECIATION***

**Ocean acidification**

- decrease of $OH^-$ and $CO_3^{2-}$ ions
- increase of $Ca^{2+}$ concentration by impacting biological calcification and carbonate dissolution

Implications:

- Increase of **free metal ion - most toxic specie**
- Competition of $H^+$ and $Ca^{2+}$ ions for binding sites on ligands and organisms' cells

**Free ion increase by the year 2100:**

| Element | Increase factor |
|---|---|
| **Al** | 2.1 |
| **Fe** | 2.4 |
| **Cu** | 1.5 |
| **Pb** | 2.0 |
| **REE** | 2-4 |

## Inorganic speciation

- Most affected are **carbonate** complexed elements: e.g., $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Pb^{2+}$, $UO_2^{2+}$, $Zn^{2+}$, REE and **hydroxides**: e.g., $Al^{3+}$, $Cr^{3+}$, $Fe^{2+}$
- Not affected: Chloride complexed $Cd^{2+}$, $Hg^{2+}$ or $Cu^+$

Millero et al., 2009, *Oceanography*; Stockdale et al., 2016, *ES&T*

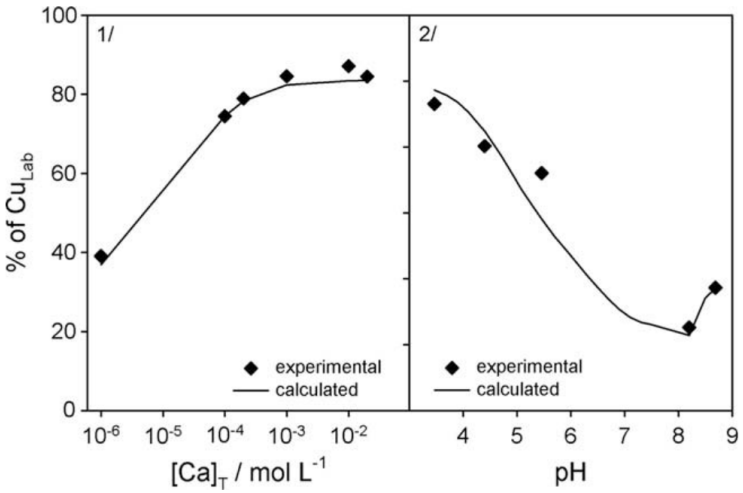
## Organic speciation

- **Less experimentally studied and less reliable modelling**
- Elements dominated by organic speciation: Cd, Co, Cu, Fe, Pb, Zn

Experimental evidences combined with modelling:

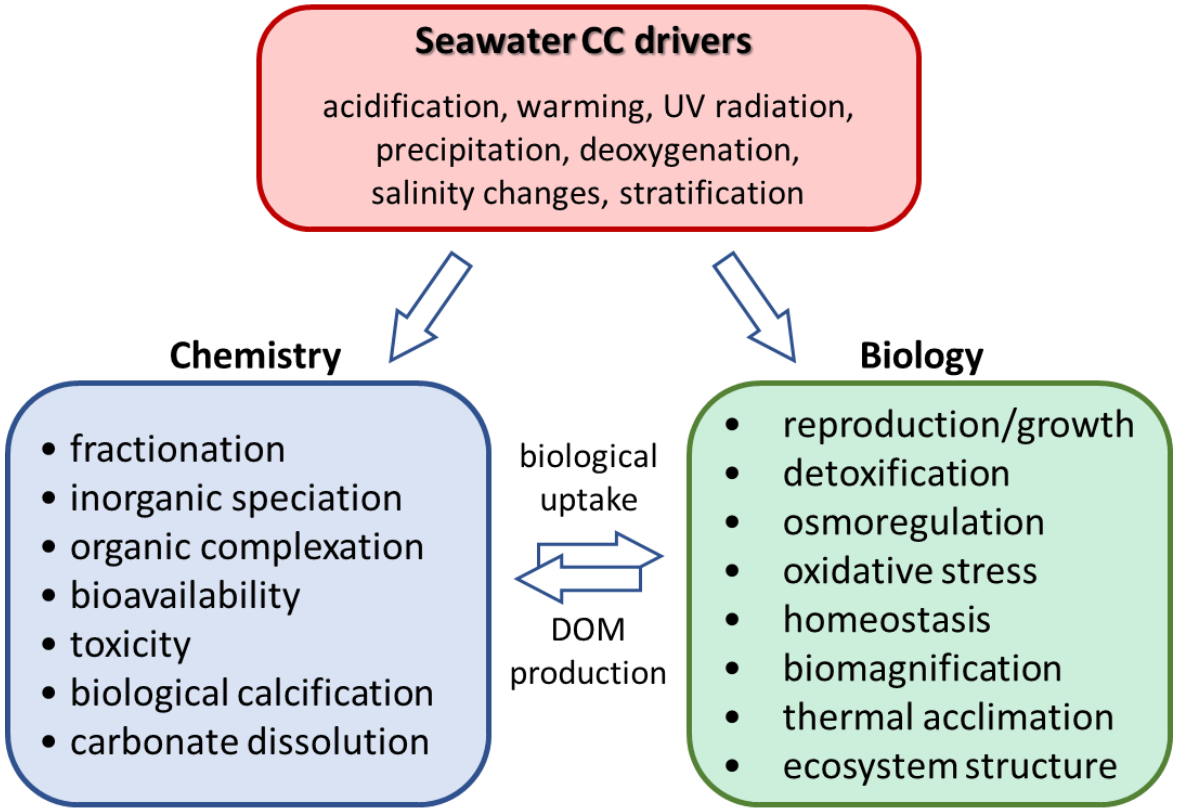
**Concentration and composition of organic matter** may be more important for Cu speciation than pH

Gledhill at al., 2015, *Marine Chemistry*



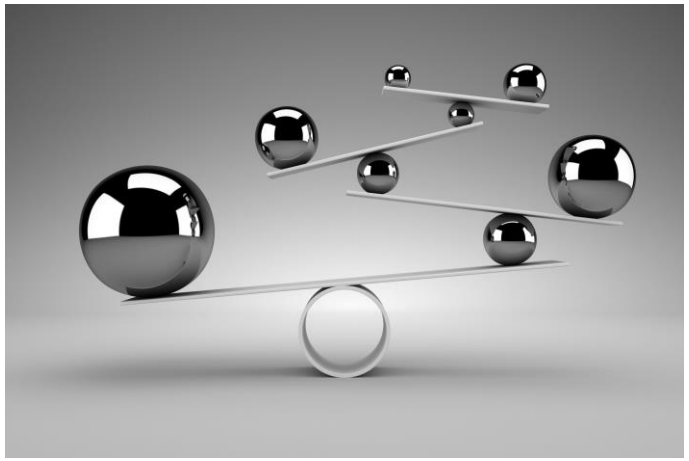

Louis, et al., 2009, *Marine Environmental Research*

# 3. Impacts on **biological responses/sensitivity**




**Biological responses and net effects depend on:**

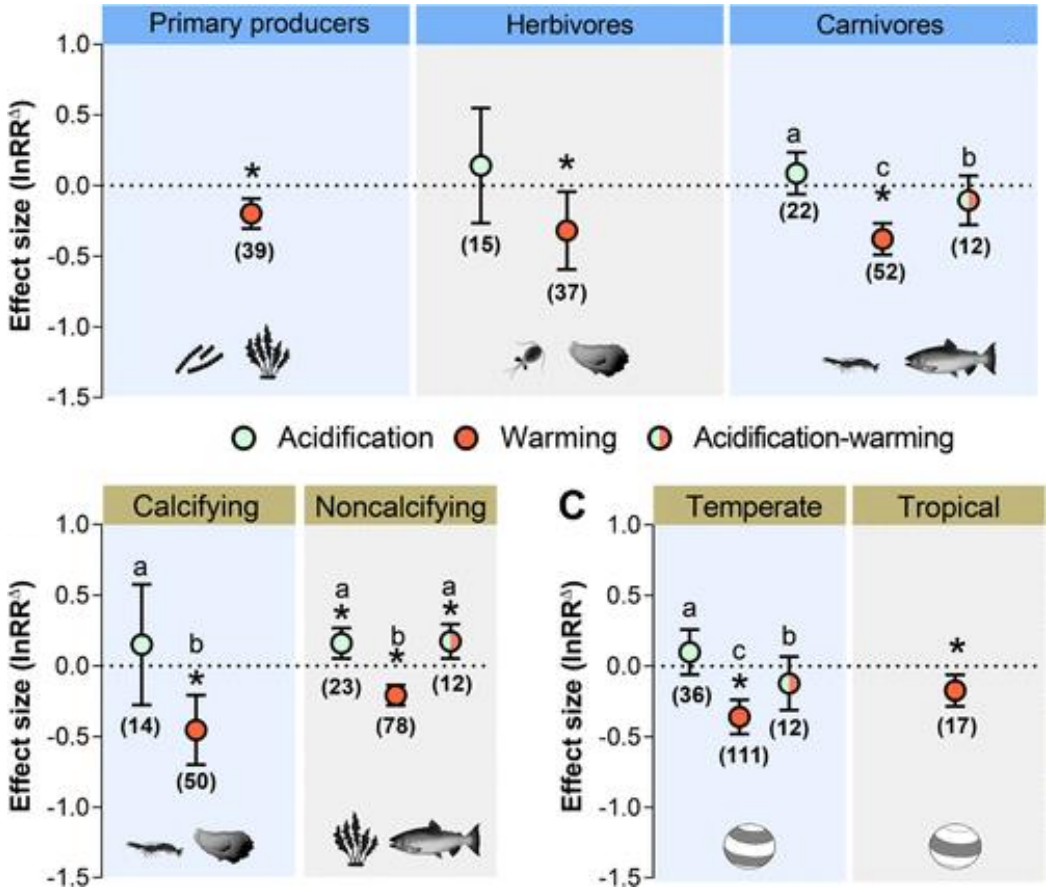
- Climate change driver
- Trace metal
- Species
- Life stage
- Combination of drivers (synergistic/antagonistic)
- Geographical region
- Adaptation



**Biological response: CC drivers (+) TM contaminants**

# 3. Impacts on **biological responses/sensitivity**

Effects of **ocean acidification** and/or **warming** on **Hg toxicity** in marine organisms across trophic levels:




Wei et al., 2023, *Environmental Science & Technology*

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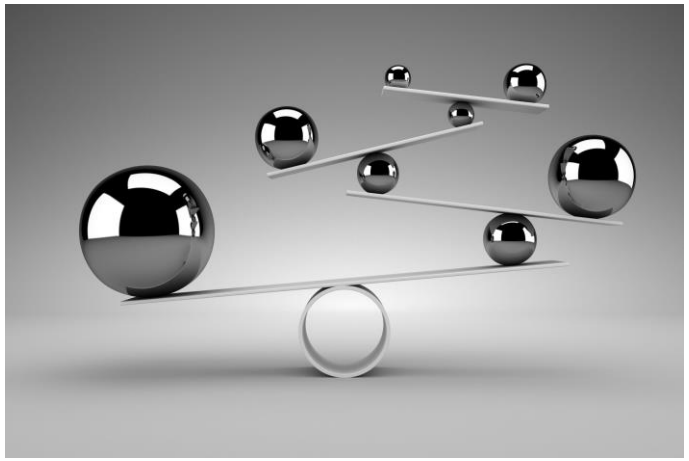

**Biological response: CC drivers (+) TM contaminants**

# Summary

- **Anthropogenic emissions** of trace metals have increased exponentially, both in **volume and variety** of metal compounds
- The **toxicity** of trace metals in seawater depends on their **chemical forms**, **how organisms interact** with them, and **environmental conditions** that influence exposure
- Their distribution and **cycling** in the marine environment are dynamic, and shaped by different **physical, chemical, and biological processes**
- **Climate change** is adding complexity by altering trace metal **sources**, **transport**, **and biogeochemical cycles**, as well as the **biological response** to combined stressors

**Understanding these interactions is essential to manage trace metal impacts on coastal ecosystems**

**Photo: Zadar Marina, Croatia**

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# THANK YOU FOR YOUR ATTENTION!

Photo: Krka River estuary, Croatia