Effect of effluent dissolved organic matter on trace metals sorption by mineral particles in aquatic systems under strong urban pressure

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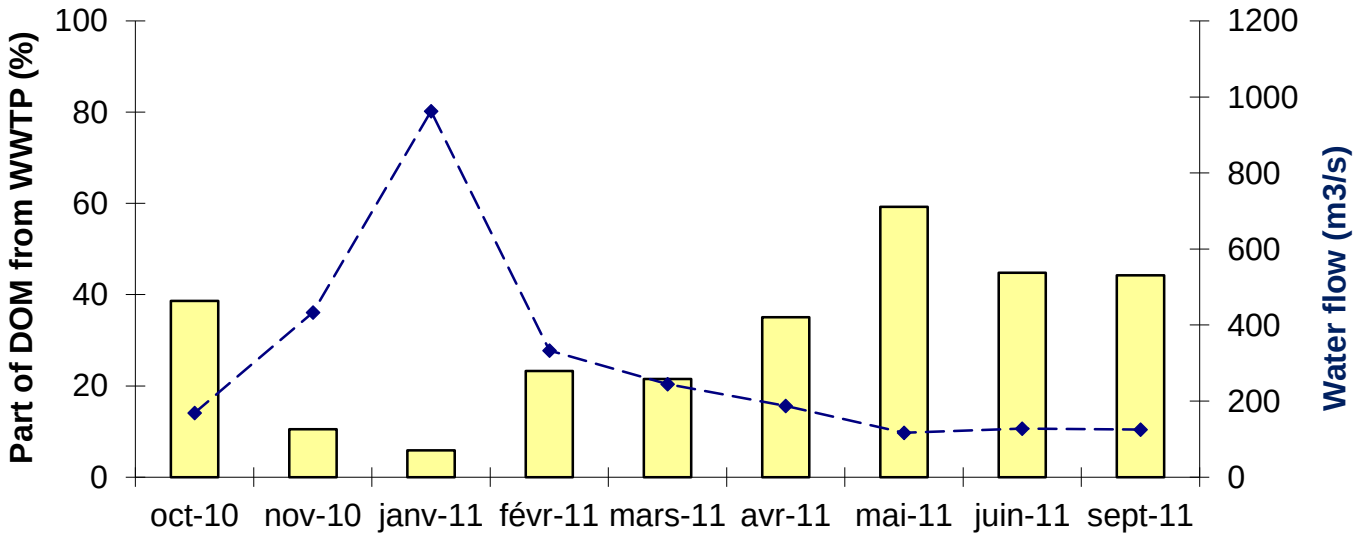
Why studying effluent dissolved organic matter (EfDOM)?

- Organic matter from WWTPs
- Present in anthropized aquatic environment
  - 10 to 60% of the DOM in the Seine River is from the WWTP depending on the flow (low-flow period)



Matar *et al.* (2015) Environ Sci Pollut Res 22:19461–19472

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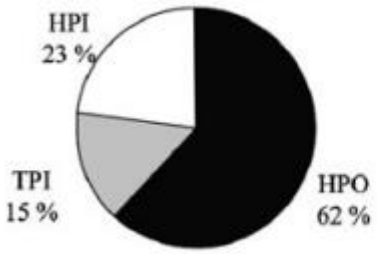
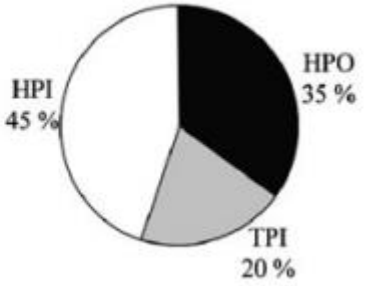
  - 10 to 60% of the DOM in the Seine River is from the WWTP depending on the flow (low-flow period)
- Physico-chemical properties different from natural DOM
  - More hydrophilic
    - 20 to 40% of hydrophilic DOM **before** Paris
    - 50 to 55% of hydrophilic DOM **after** Paris

DOM from river



EfDOM



Pernet-Coudrier *et al.* (2011) Biogeochemistry 106:89–106

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    - 20 to 40% of hydrophilic DOM **before** Paris
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  - More nitrogen and sulfur groups
  - Lower molecular weight

Pernet-Coudrier *et al.* (2011) Biogeochemistry 106:89–106

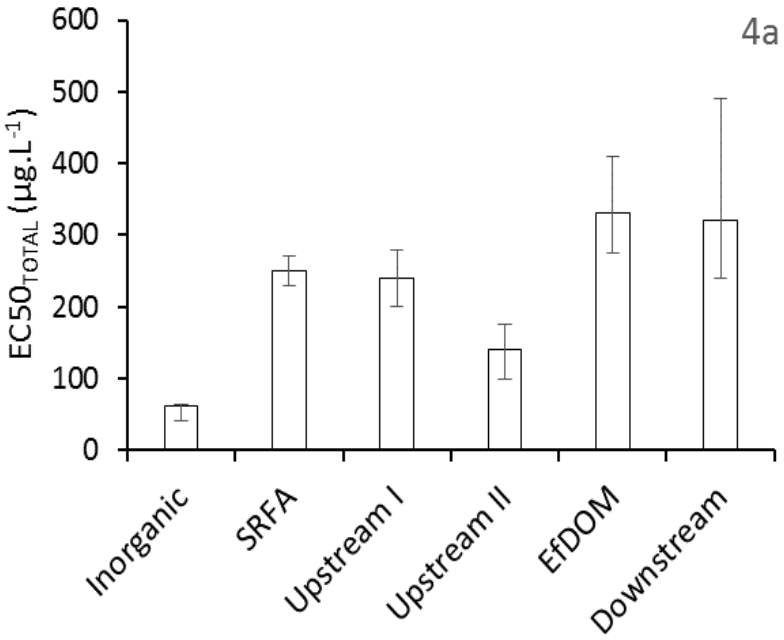
Why studying effluent dissolved organic matter (EfDOM)?

- Strong influence on the **speciation** of the trace metals
  - 80 to 90% of lead and mercury are binded to EfDOM after Paris conurbation in the Seine River
  - Decrease of the free copper (-70%) after Paris conurbation

Matar *et al.* (2015) Environ Sci Pollut Res 22:19461–19472

Why studying effluent dissolved organic matter (EfDOM)?

- Strong influence on the **speciation** of the trace metals
- Strong influence on the **biodisponibility** of the trace metals
  - Copper EC_{50} on *daphnia magnae* with different DOM



⇒ **Decrease** of the copper biodisponibility and toxicity **with EfDOM**

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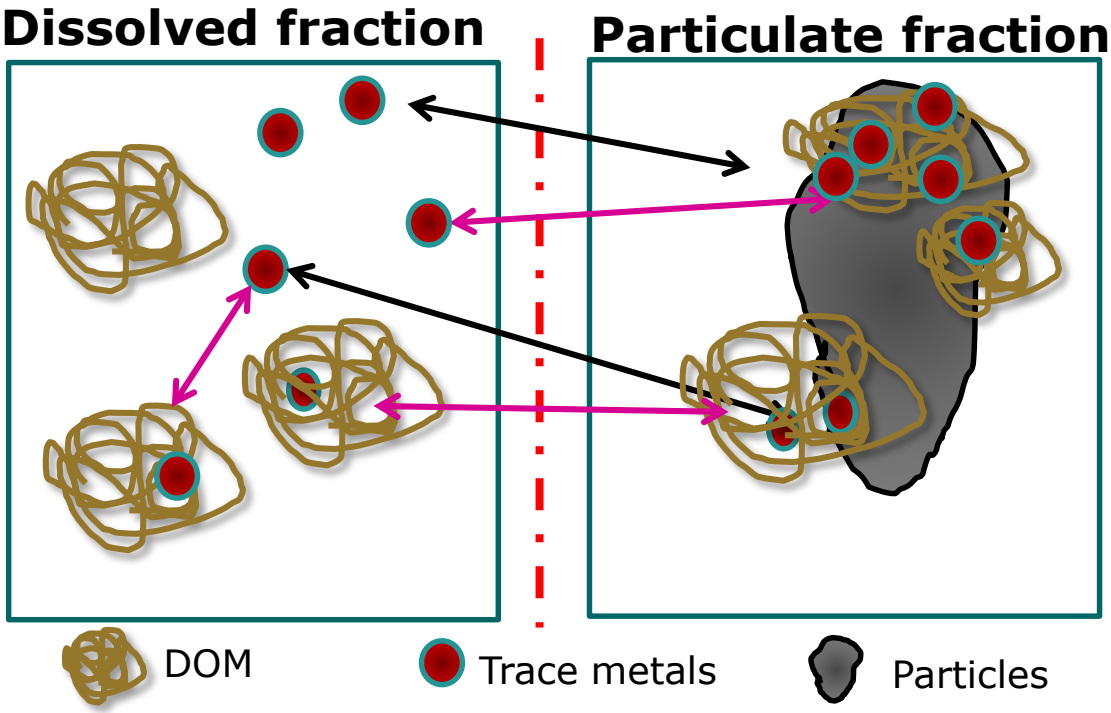
Influence of DOM on the trace metals fate in aquatic systems

- Sorption/desorption onto suspended solids



- Studies focused on natural DOM and natural particles

Objectives

1. To characterize EfDOM sorption onto mineral particles
   - Natural DOM: Suwanee River Fulvic Acid (SRFA)
   - EfDOM: from WWTPs

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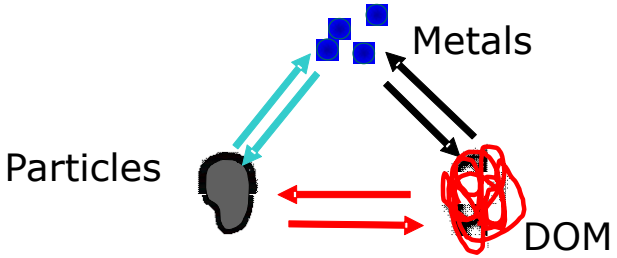
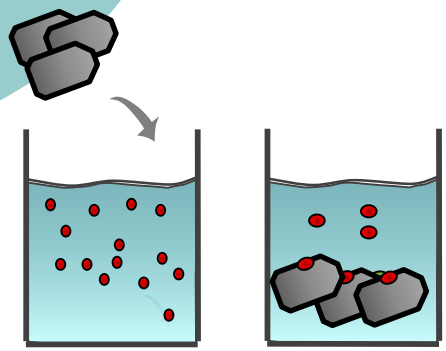
2. To characterize metals sorption onto mineral particles with or without DOM
   - Natural DOM: Suwanee River Fulvic Acid (SRFA)
   - EfDOM: from WWTPs

Methodology



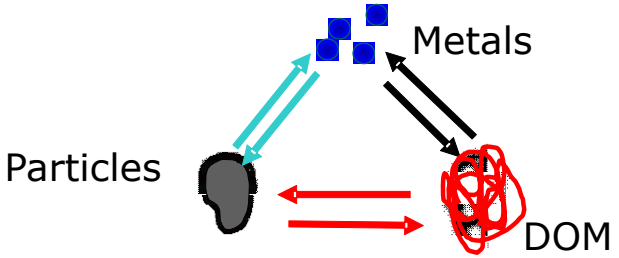


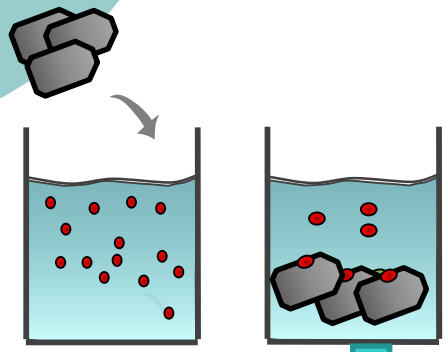
Under stirring during 72 hours at 19°C

- DOM (10mgC/L)
  - Without DOM
  - SRFA
  - EfDOM from WWTP

- Adsorbant (0-500mg/L)
  - Montmorillonite
  - Goethite

Methodology





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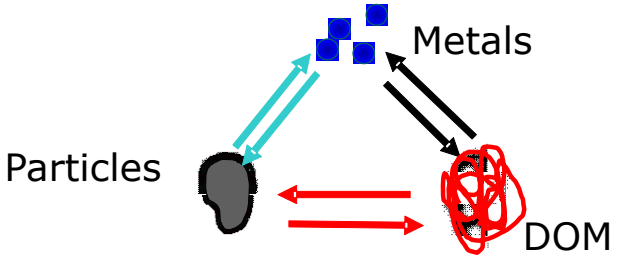
  - Without OM
  - SRFA
  - EfDOM from WWTP

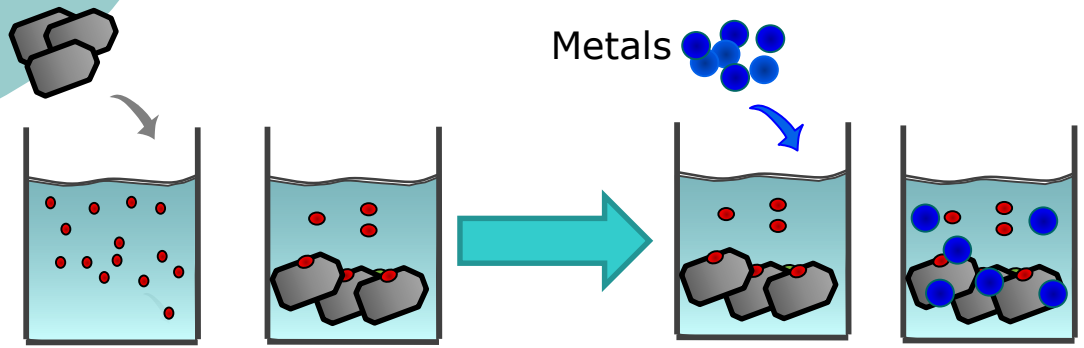
- Adsorbant (0-500mg/L)
  - Montmorillonite
  - Goethite

- Filtration on GF/F 0.7 µm
- DOC analysis

1. To characterize DOM sorption onto mineral particles

Methodology





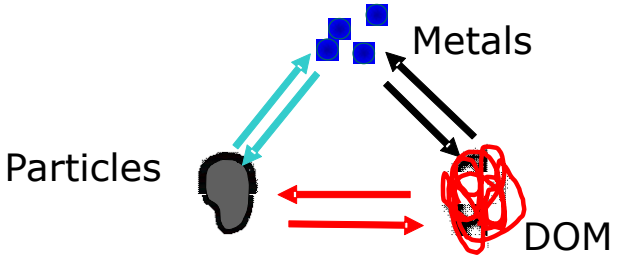
Under stirring during
72 hours at 19°C

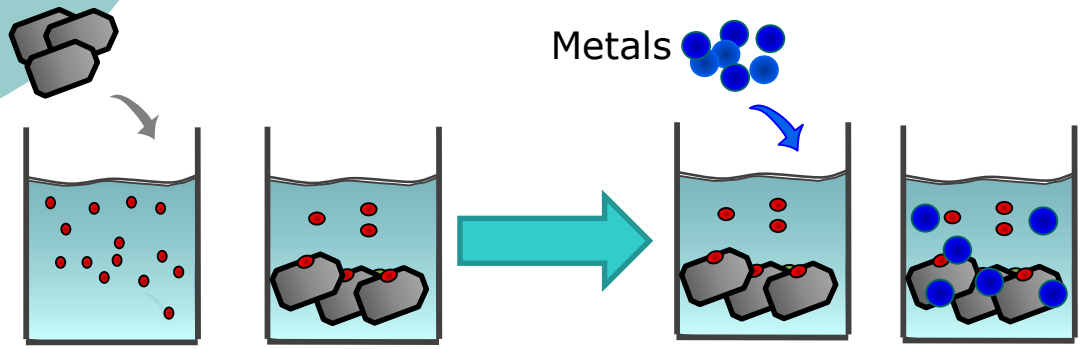
- DOM (10mgC/L)
  - Without DOM
  - SRFA
  - EfDOM from WWTP

- 7 metals (Cd, Co, Cu, Ni, Pb, V and Zn)
  1 metalloid (As)

- Adsorbant (0-500mg/L)
  - Montmorillonite
  - Goethite

Methodology





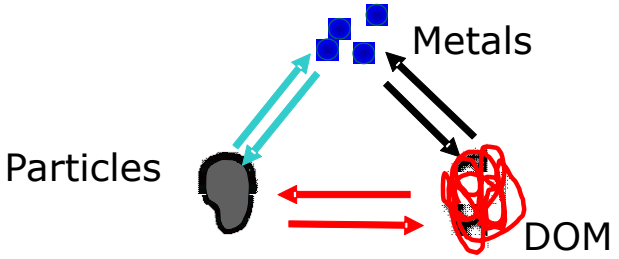
- Filtration on cellulose acetate
- ICP-AES analysis

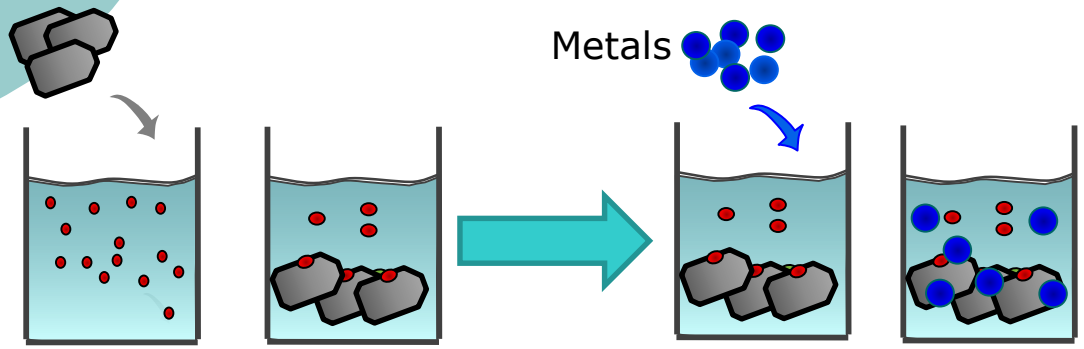
Dissolved metals

- DOM (10mgC/L)
  - Without DOM
  - SRFA
  - EfDOM from WWTP

- Adsorbant (0-500mg/L)
  - Montmorillonite
  - Goethite

Methodology

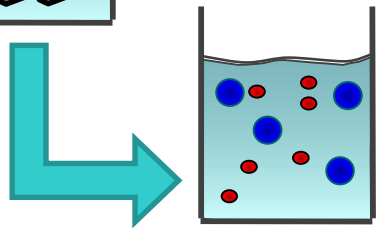




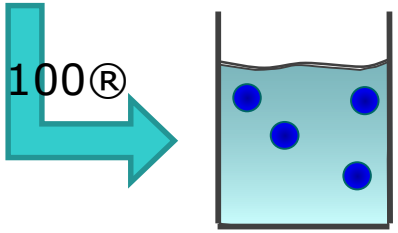
- DOM (10mgC/L)
  - Without DOM
  - SRFA
  - EfDOM from WWTP

- Adsorbant (0-500mg/L)
  - Montmorillonite
  - Goethite

- Filtration on Chelex 100®
- ICP-AES analysis



Dissolved metals

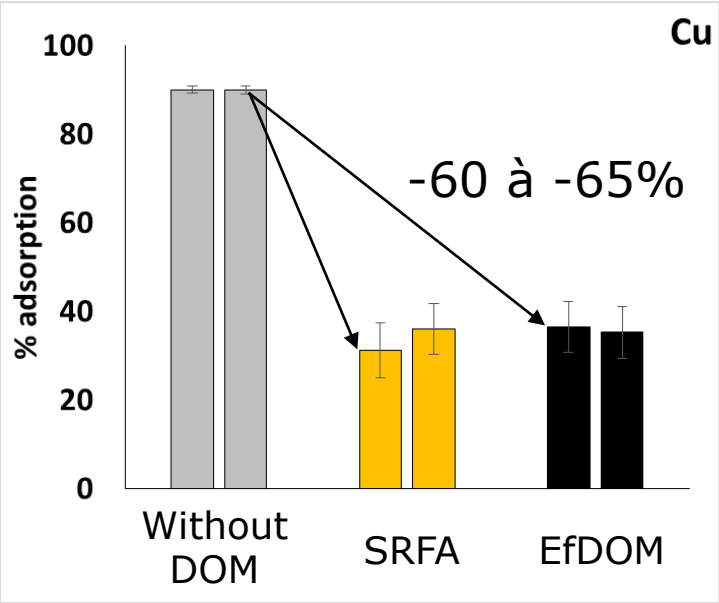


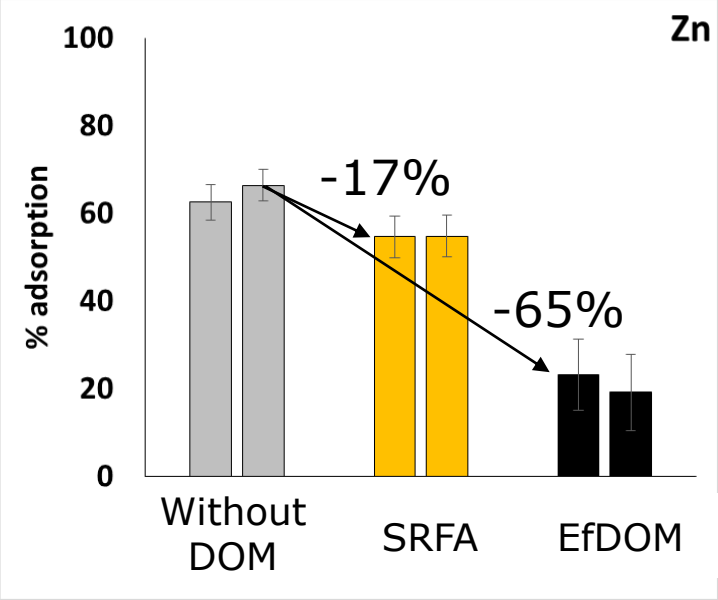
Inert metals

2. To characterize metals sorption onto mineral particles with or without DOM

Influence of DOM on Cu and Zn sorption on montmorillonite

Sorption with or without DOM





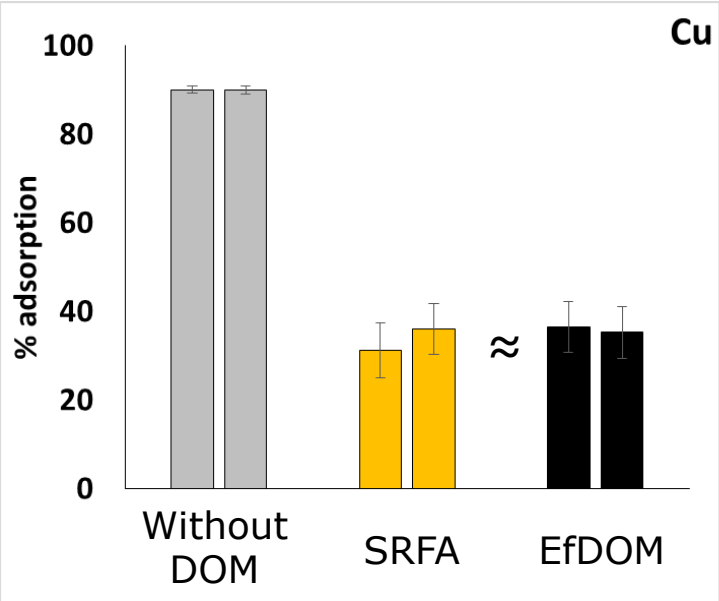
Copper and zinc

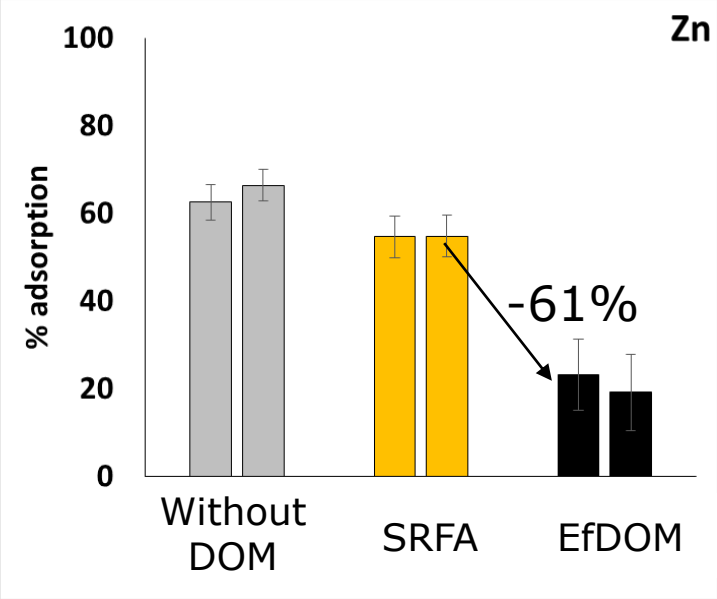
- Less sorption with DOM

1. **Retention in dissolved fraction → complexes DOM-Cu or DOM-Zn**
2. **Competition DOM vs. Cu and Zn for surface sites**

Influence of DOM on Cu and Zn sorption on montmorillonite

Sorption with SRFA or EfDOM





Copper

➢No influence of the type of DOM

Zinc

➢ Influence of the type of DOM => less sorption with EfDOM

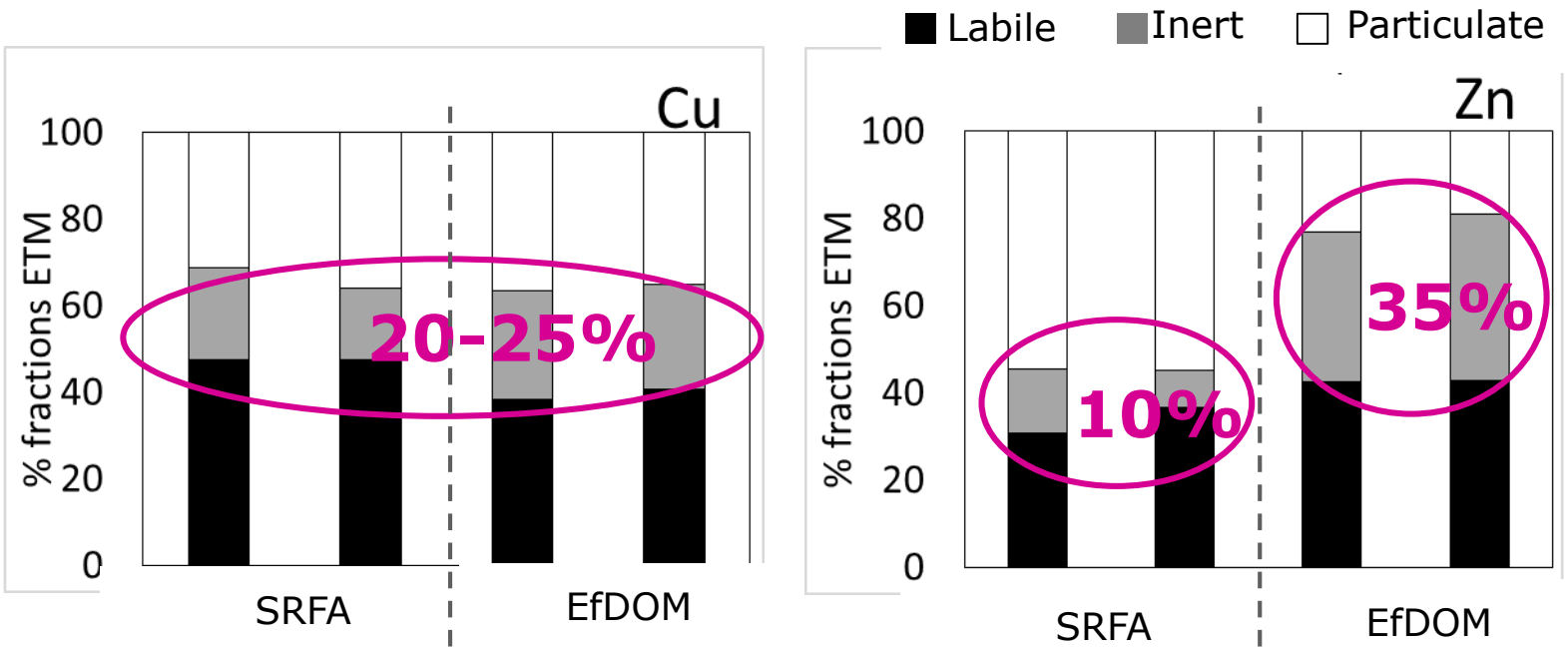
Fate of Cu and Zn

➢ Between 65 and 80% in the dissolved fraction

➢ What speciation? Free or complexed?

Influence of DOM on Cu and Zn sorption on montmorillonite

Speciation of Cu and Zn: comparison SRFA and EfDOM

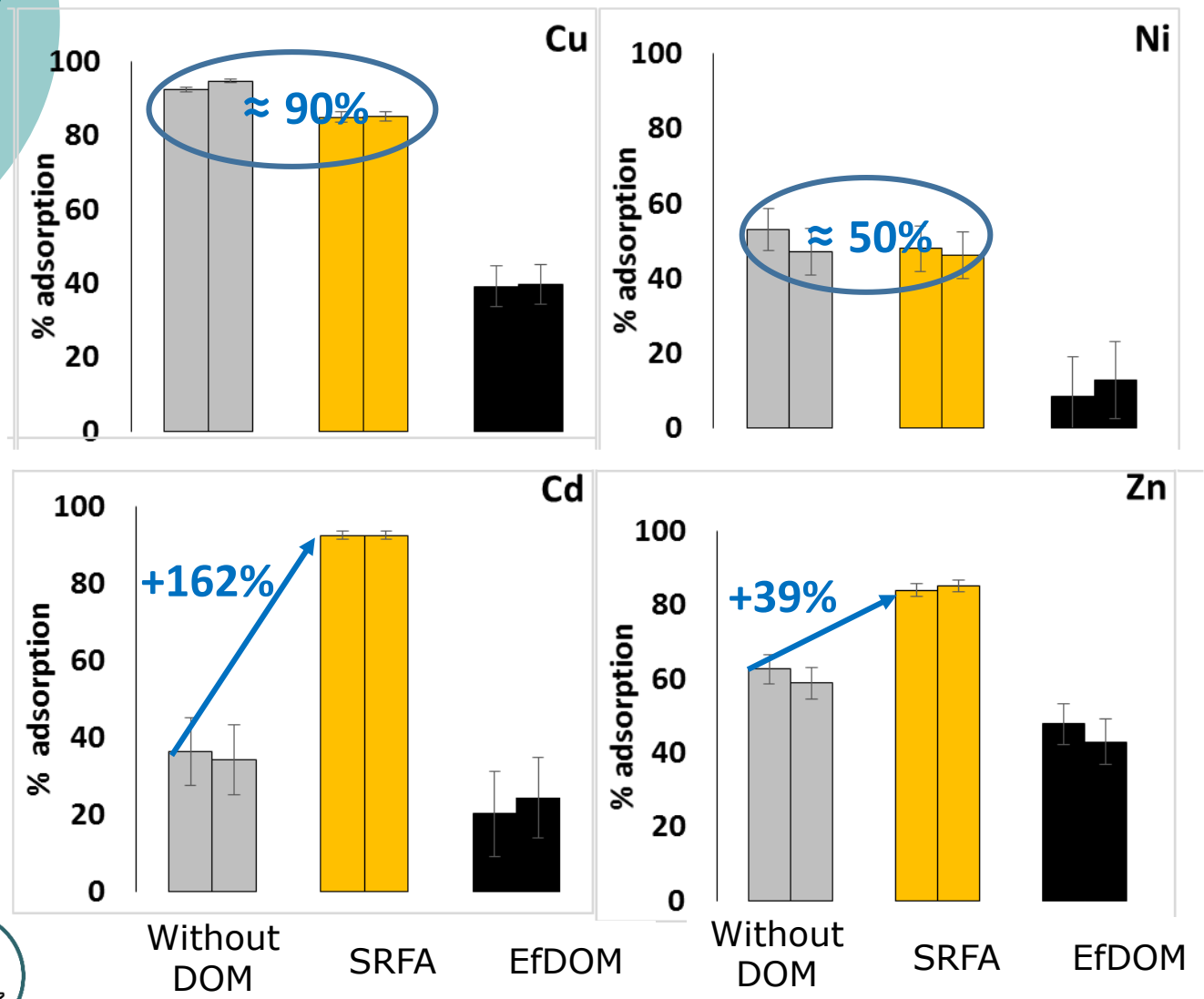


- Cu speciation is similar with SRFA and EfDOM
- Zn inert fraction is higher with EfDOM

With EfDOM, retention of complexes DOM-Zn in dissolved fraction

Influence of DOM on metals sorption on goethite

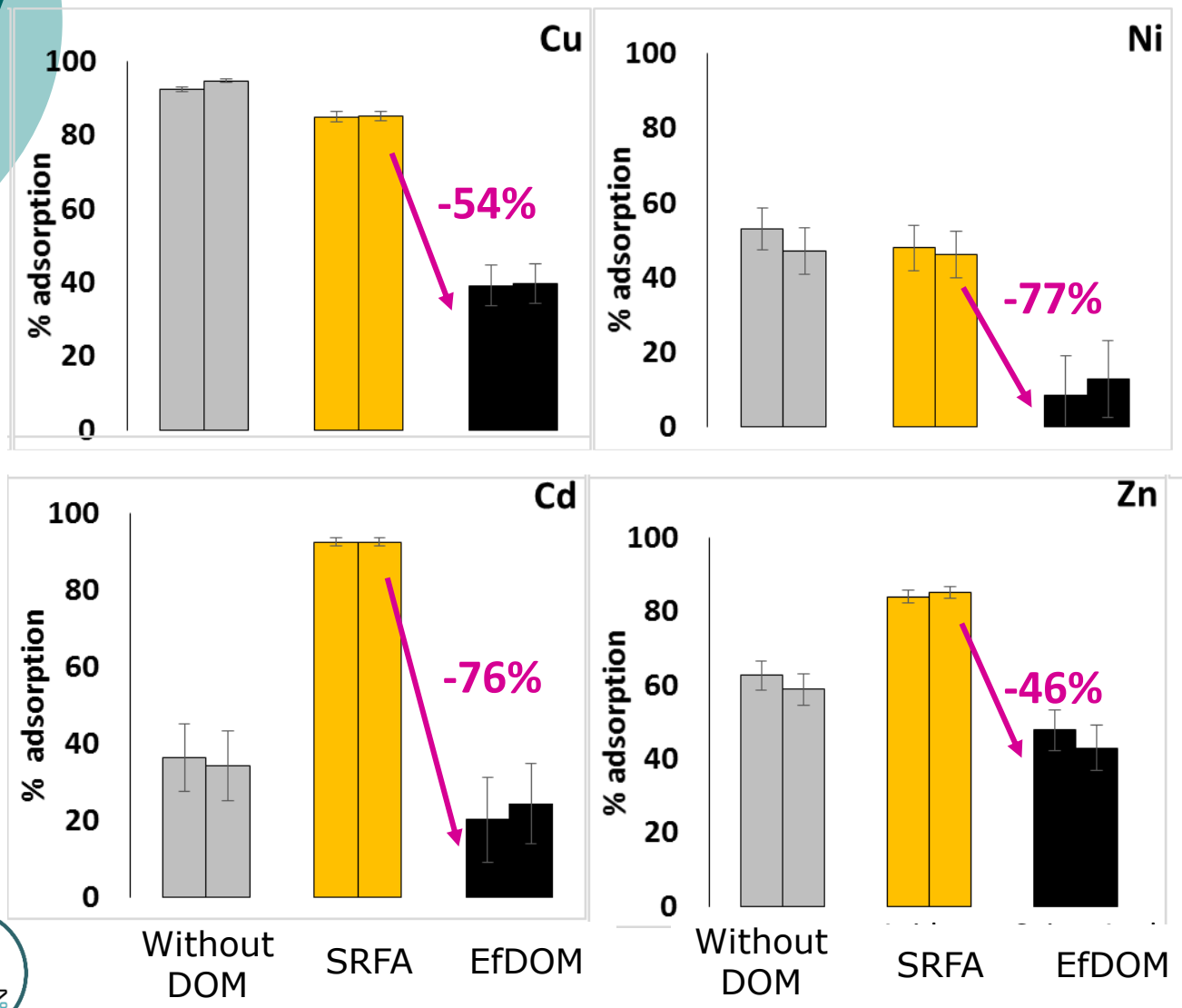
Sorption without DOM or with SRFA



- (≈) Cu and Ni
- (+) Cd and Zn

Influence of DOM on metals sorption on goethite

Sorption with SRFA or EfDOM



- Less adsorption with EfDOM

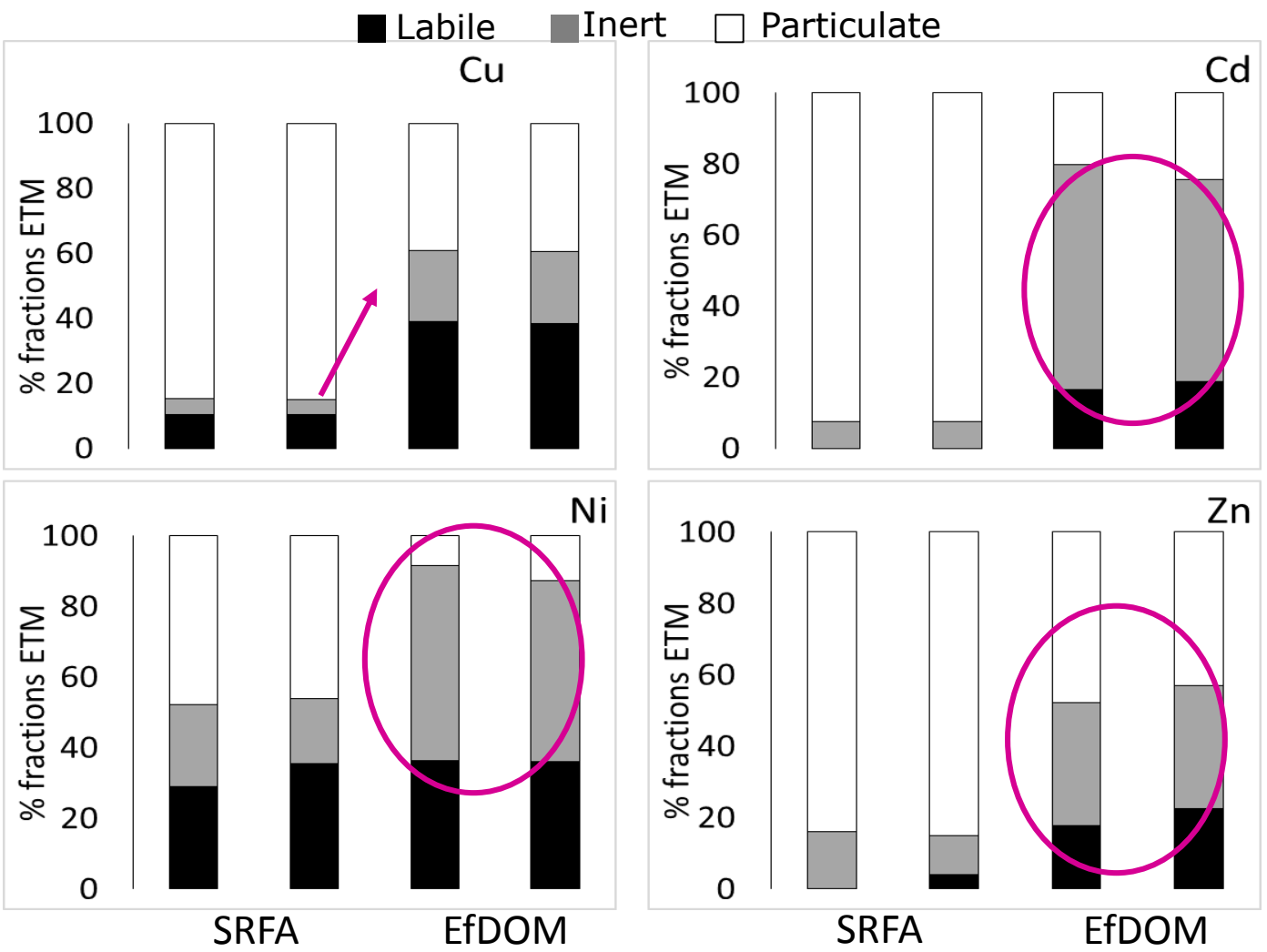
Influence of DOM on metals sorption on goethite

Cu

Increase of labile fraction with EfDOM

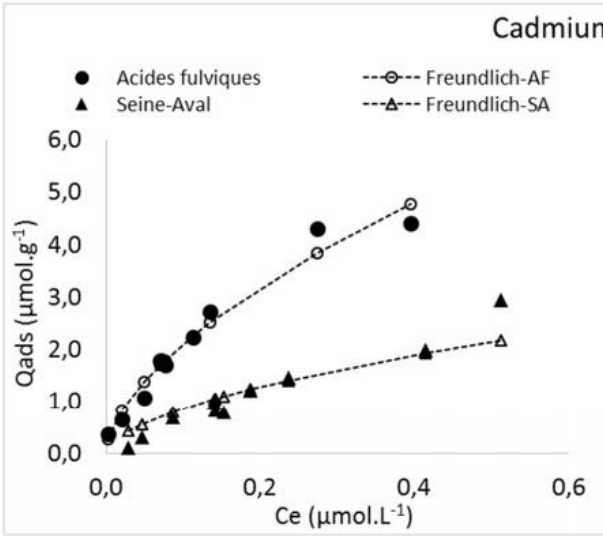
Cd, Ni and Zn

Less sorption due to the retention in dissolved fraction by complexation



Conclusion and outlook

- **EfDOM strongly influence the dissolved/particulate partition of metals**
  - DOM and in particular EfDOM maintain metals in dissolved fraction by:
    - Complexation and/or
    - Competition for surface sites
- **EfDOM strongly influence the speciation of metals in dissolved fraction**
  - Increase of zinc labile fraction with EfDOM and montmorillonite by complexation
  - Strong increase of copper labile fraction with goethite
- **Complete sorption isotherms => to model the constants describing dissolved/particulate partition of metals**
  - Explain the mechanisms responsible of the speciation



Thank you for your attention

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Influence of DOM on the trace metals fate in aquatic systems

- Sorption/desorption onto suspended solids

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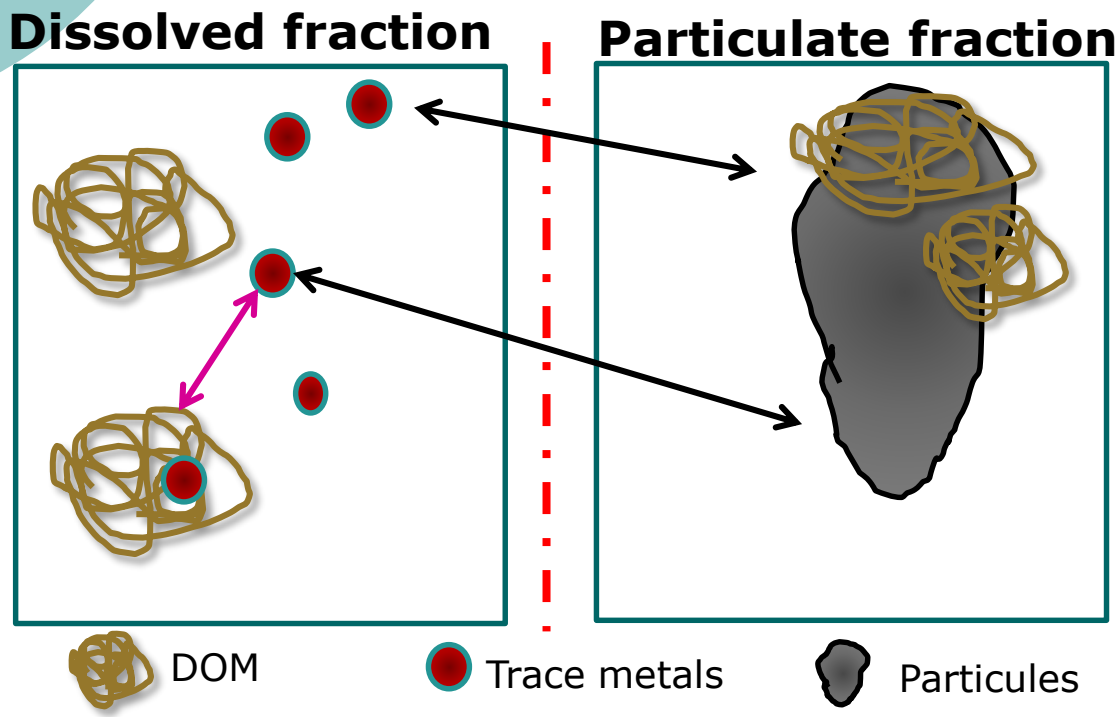
   (Moon *et al.*, 2003)



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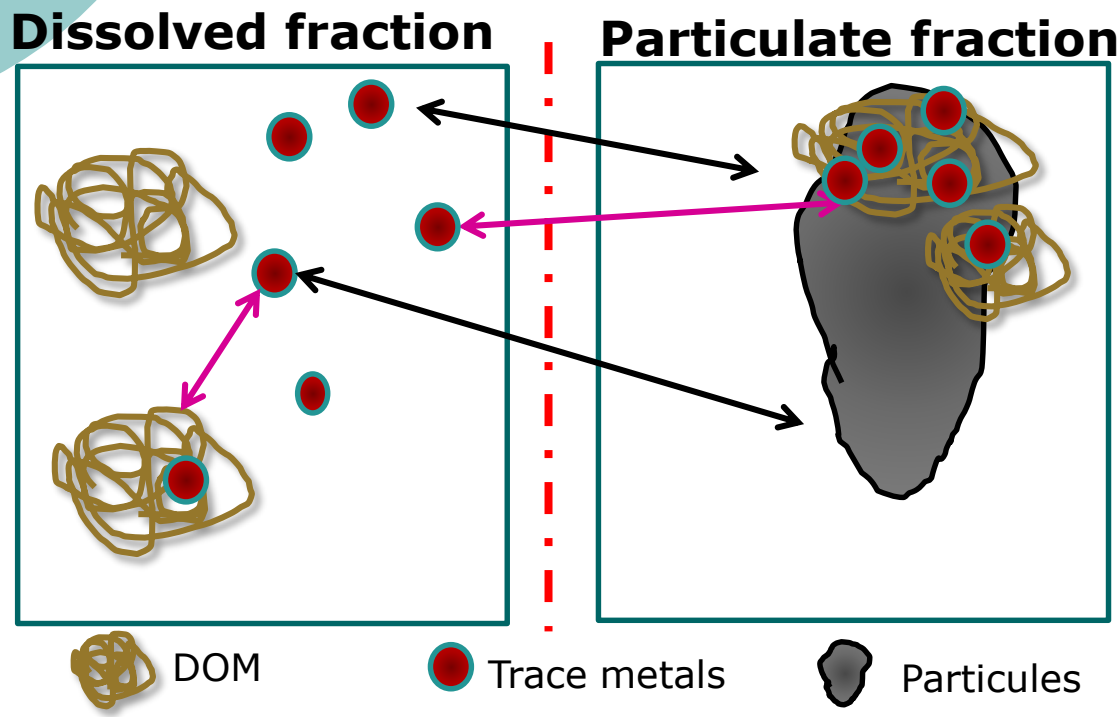

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2. **Increase of the fixation ability**
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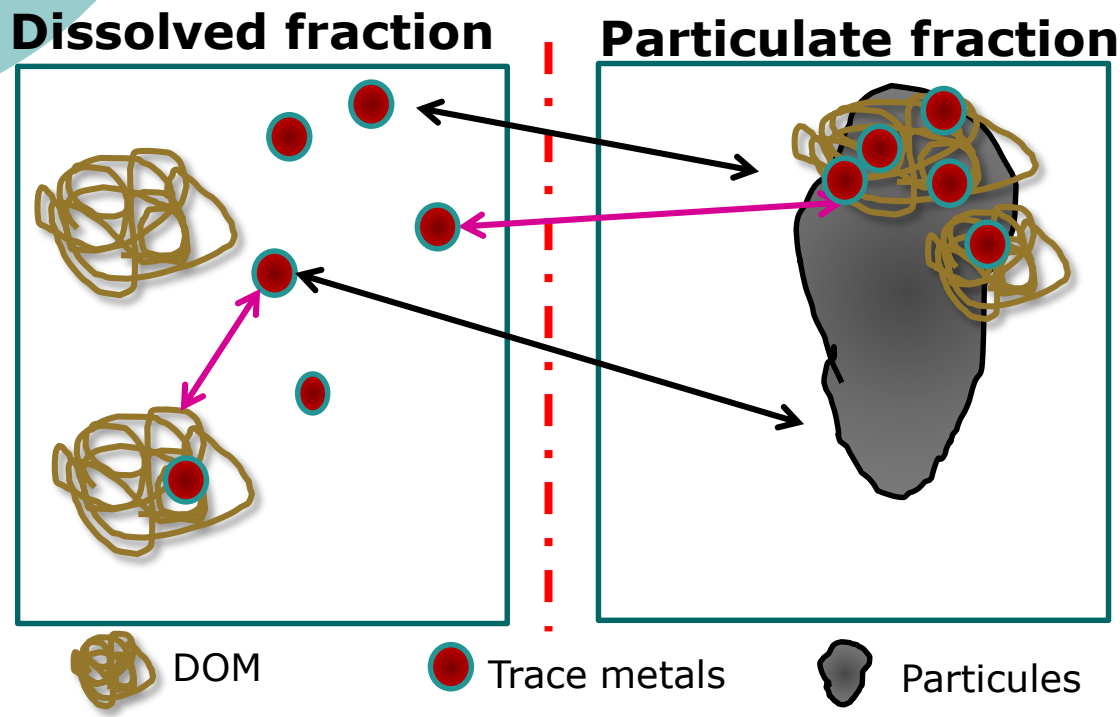

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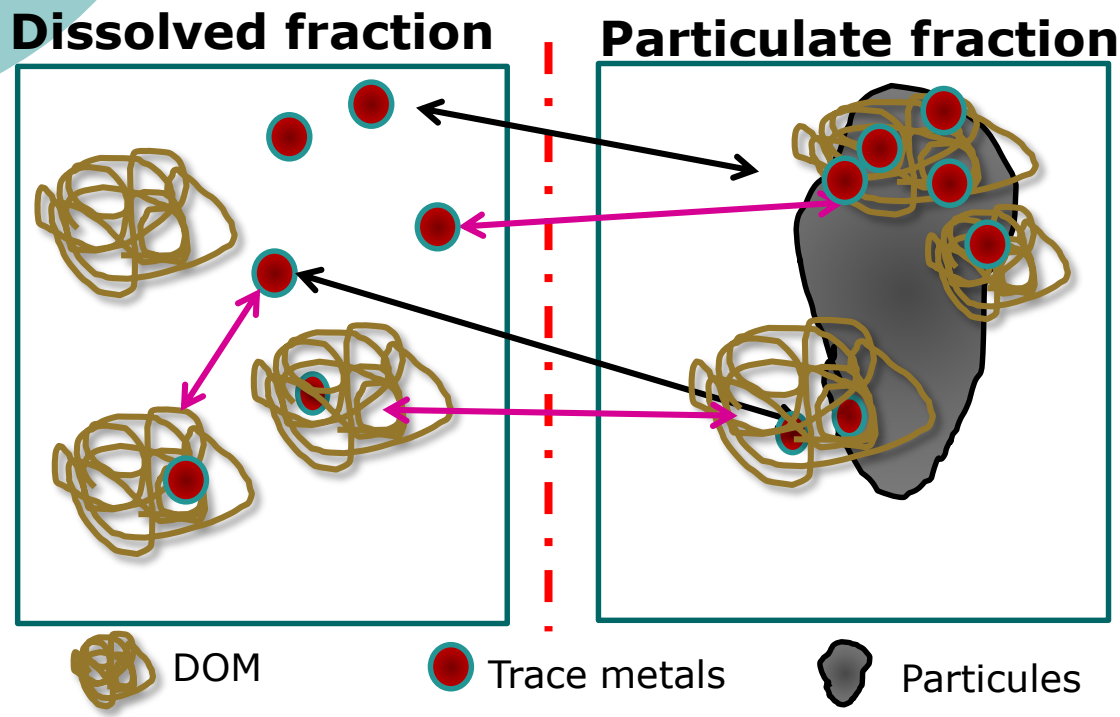

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4. **Adsorption of metals on DOM**
   (Wu *et al.*, 2011)

Influence of DOM on the trace metals fate in aquatic systems

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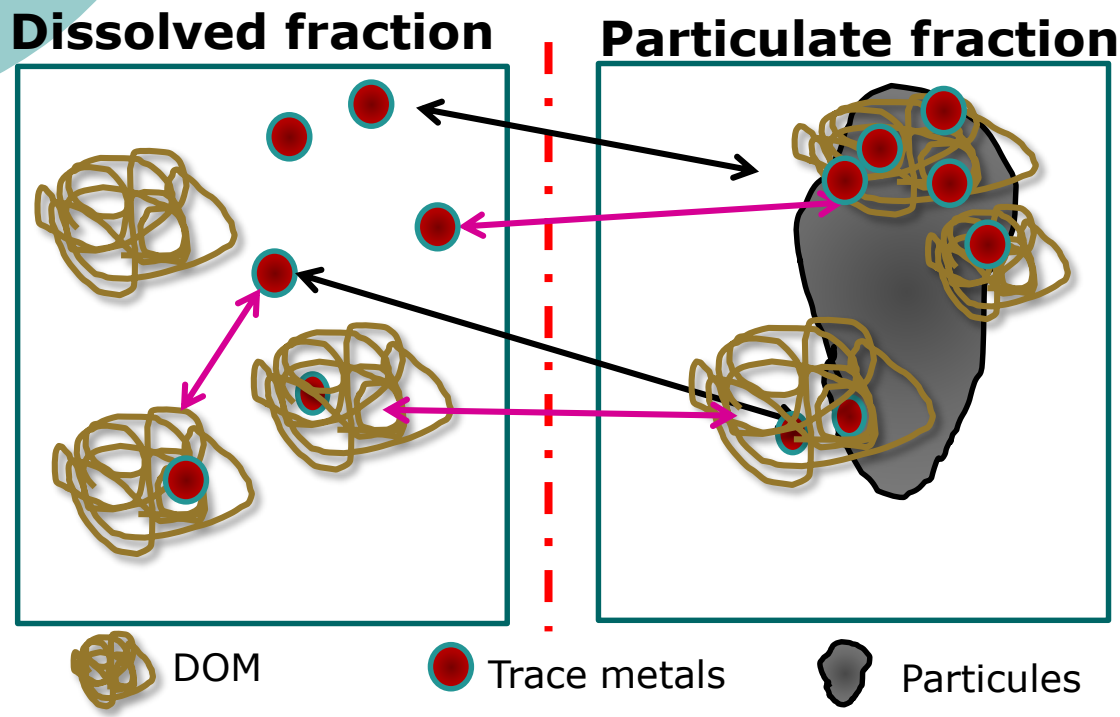

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5. **Pores obstruction**
   (Newcombe *et al.*, 2002 ; Li *et al.*, 2003)