TRACE ELEMENTS DISTRIBUTION AND MOBILITY IN ESTUARINE SEDIMENTS OF THE KRKA RIVER (CROATIA)

Nuša Cukrov, Cédric Garnier, Duc Huy Dang, Ana-Marija Cindrić, Dario Omanović, Neven Cukrov
Why do we study trace metals in the sediment?

- Inorganic contaminants
- Non-degradable
- Bioaccumulation and biomagnification

Gaillardet et al., 2013
Sediment = sink for contaminants?

Sediment = potential secondary source of contaminants!
Sediment = sink for contaminants?

Mineralization of organic matter
Pore water

- The chemistry of sediment pore waters provides important information regarding chemical reactions in sediments.
- Pore water analyses are used for diagenetic studies, sediment quality assessment and toxicity identification.
Study area

- Krka River – karstic river, eastern coast of the Adriatic Sea (Croatia)
- Krka National Park
- Low input of trace metals, suspended particulate matter and organic carbon by the river.
Krka River estuary

- Length: 23 km
- Low tidal range and sheltered geography
- Permanent vertical stratification:

  - **Brackish layer**
  - **Freshwater - seawater interface**
  - **Seawater layer**
Krka River estuary

Old factory of electrodes and ferroalloys

Phosphate transhipment port

Nautical marina and overhaul shipyard
Research objectives

1. Define main source of pollution within the estuary

- **Surface sediment samples** (5 cm)
- 40 sampling location
- Major/minor/trace elements
Research objectives

1. Define main source of pollution within the estuary

2. Gain information about vertical distribution and mobility of trace metals in estuarine sediments
   - Classical ex situ method (extracting porewater by centrifugation),
   - In situ application of DGT (diffusive gradients in thin films) probes.
1st objective

Methods

• Sampling - Gravity corer (Uwitec)
• Freezing, lyophilization and sieving <2mm
• Hg - untreated samples - AMA 254 (LECO Corporation)
• Al, As, Ba, Be, Bi, Cr, Cs, Cu, Cd, Co, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, Zn – Aqua Regia digestion - HR ICP-MS (Element 2, Thermo)
• Interpolation method – Inverse distance weighted (Golden Software Surfer)
### 1st objective Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Lower Estuary</th>
<th>Upper Estuary</th>
<th>ERL</th>
<th>ERM</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>8.14 - 39.6</td>
<td>5.43 - 13.6</td>
<td>8.2</td>
<td>70</td>
</tr>
<tr>
<td>Cd</td>
<td>0.11 - 11.2</td>
<td>0.20 - 0.53</td>
<td>1.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Cr</td>
<td>31.3 – 129</td>
<td>30.1 - 72.8</td>
<td>81</td>
<td>370</td>
</tr>
<tr>
<td>Cu</td>
<td>12.4 – 132</td>
<td>9.27 - 30.8</td>
<td>34</td>
<td>270</td>
</tr>
<tr>
<td>Pb</td>
<td>21.1 - 665</td>
<td>18.0 - 52.1</td>
<td>46.7</td>
<td>218</td>
</tr>
<tr>
<td>Hg</td>
<td>0.125 - 12.4</td>
<td>0.058 - 0.397</td>
<td>0.15</td>
<td>0.71</td>
</tr>
<tr>
<td>Zn</td>
<td>47.8 – 1200</td>
<td>70.0 - 107</td>
<td>150</td>
<td>410</td>
</tr>
</tbody>
</table>

Values are expressed in μg g⁻¹

No elevated metal concentrations were found in the upper part of estuary.
### 1st objective Results

Enrichment Factor = \[
\frac{\left(\frac{\text{element}}{\text{Li}}\right)_{\text{sample}}}{\left(\frac{\text{element}}{\text{Li}}\right)_{\text{background}}}
\]

<table>
<thead>
<tr>
<th>EF</th>
<th>min</th>
<th>max</th>
<th>mean</th>
<th>Hg</th>
<th>Mn</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
<th>As</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.91</td>
<td>151</td>
<td>17.0</td>
<td>1.11</td>
<td>0.71</td>
<td>45.4</td>
<td>1.46</td>
<td>0.51</td>
<td>1.18</td>
<td>0.85</td>
<td>0.87</td>
</tr>
</tbody>
</table>

EF < 2   deficiency to low enrichment  
EF 2–5  moderate enrichment  
EF 5–20 significant enrichment  
EF 20–40 very high enrichment  
EF >40  extremely high enrichment
Main pollution sources in the lower part of estuary:

1. Former ferromanganese industry (Mn, Pb, Bi, Ba, Co, Sb, Cu, Zn),

2. Phosphate transhipment port (U, Cd, Bi, Cr, Ag, Sb, Cu, Zn),

3. Nautical marina/overhaul shipyard (Hg, As, Cu, Sb)

Values are expressed in μg g⁻¹
2nd objective - Classical Ex situ method

- Sediment core slicing and centrifugation = pore water extraction
- Inert atmosphere ($N_2$)
- Pore water filtration (0.22 μm syringe filters, cellulose acetate)
- Dissolved Organic Carbon (DOC) - TOC-$V_{CSH}$ analyser
- Major/minor/trace elements - HR ICP-MS
2nd objective - DGT passive samplers

DGT (diffusive gradients in thin films) - simple device uses a layer of binding agent impregnated in a hydrogel to accumulate dissolved substances.

- *in situ* for 94 hours
- resolution of 5 mm
- extraction in 1.5 mL 1M HNO₃
- HR-ICP-MS: Fe, Al, Mn, Ti, Co, Cr, Pb, Ti, Cu, Ni, V, Cd
2\textsuperscript{nd} objective

Results

Processes of early diagenesis control trace metal mobility
Classical diagenetic sequence:
Subsurface peak of Mn (-2 cm), followed by Fe (maximum at -8 cm) related to Mn and Fe oxyhydroxides reduction.
2nd objective Results

Profile of Co is well correlated with Mn profile, as often observed.

- **DGT**
- **Extracted porewater**
Significant gradient at the sediment/water interface

2\textsuperscript{nd} objective

Results
2nd objective
Results

• Good agreement between 2 methods
• DGT - higher resolution
• Pore water extraction – possibility to go deeper into sediment
Conclusion

Upper part → low concentrations

Šibenik Bay → anthropogenic pollution

Possible transport to the water column
Thank you!

This work is part of project MEBTRACE - *New methodological approach to biogeochemical studies of trace metal speciation in coastal aquatic ecosystems* funded by Croatian science foundation.