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

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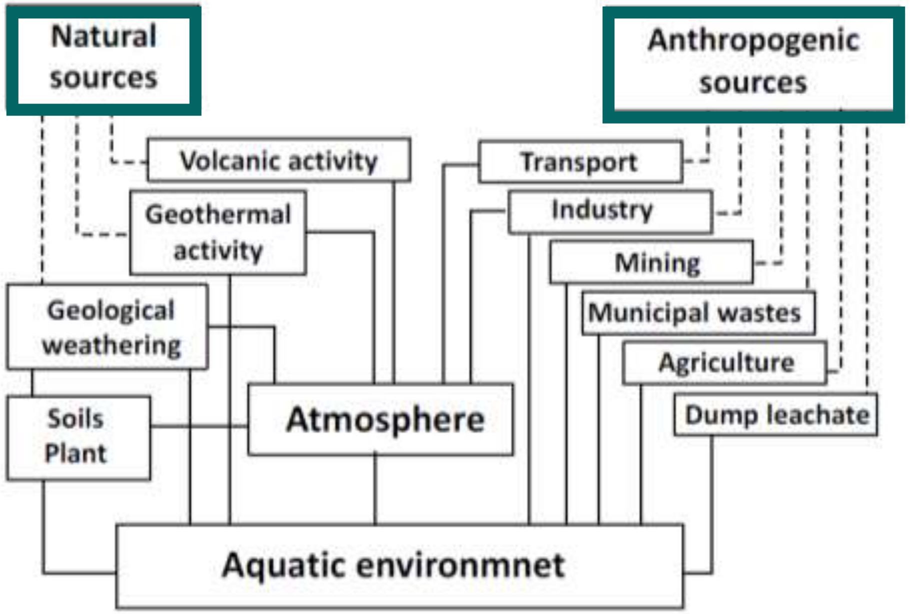
Why do we study trace metals in the sediment?

Inorganic contaminants

Non-degradable

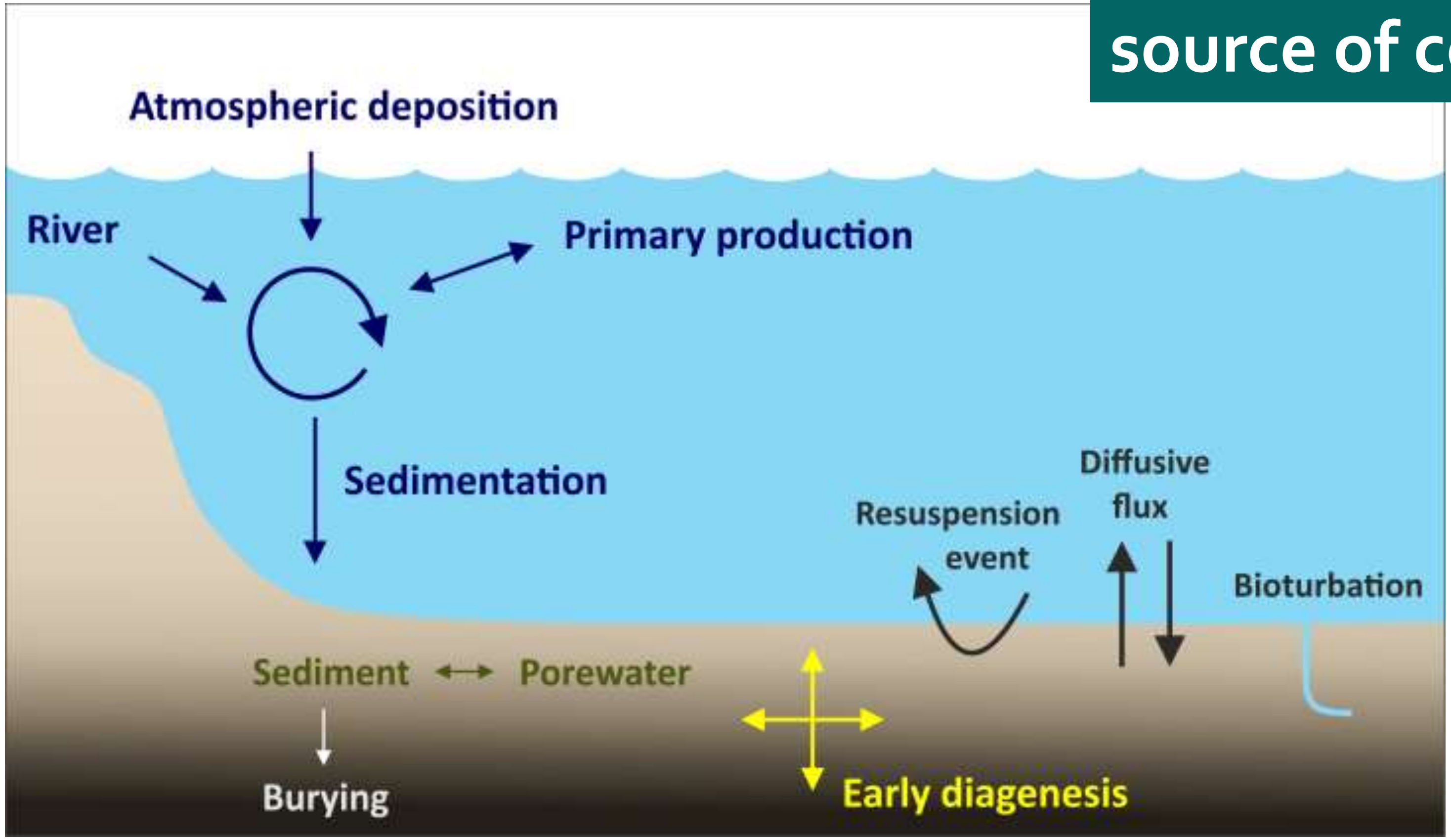
Bioaccumulation and biomagnification



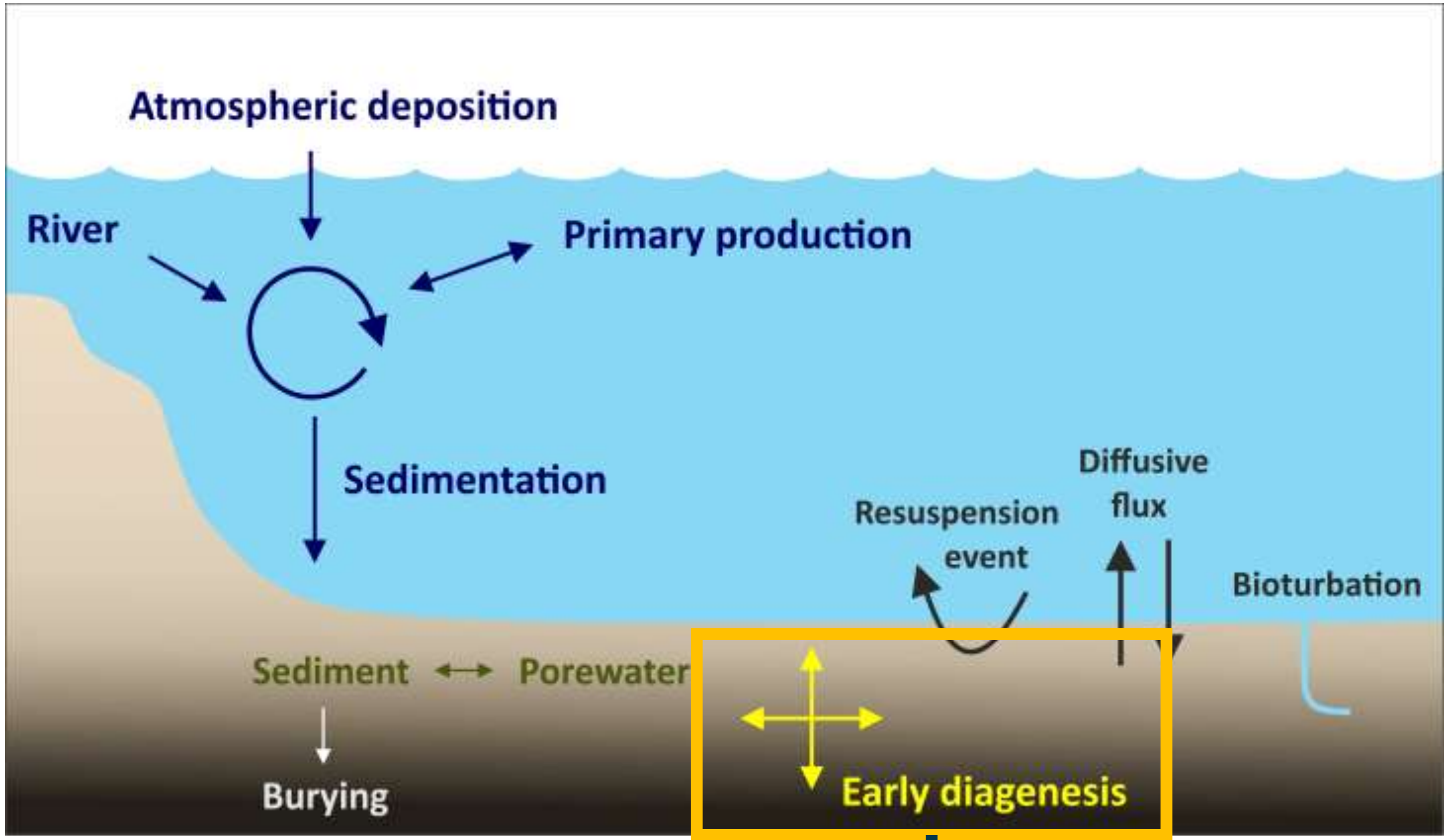
Gaillardet et al., 2013

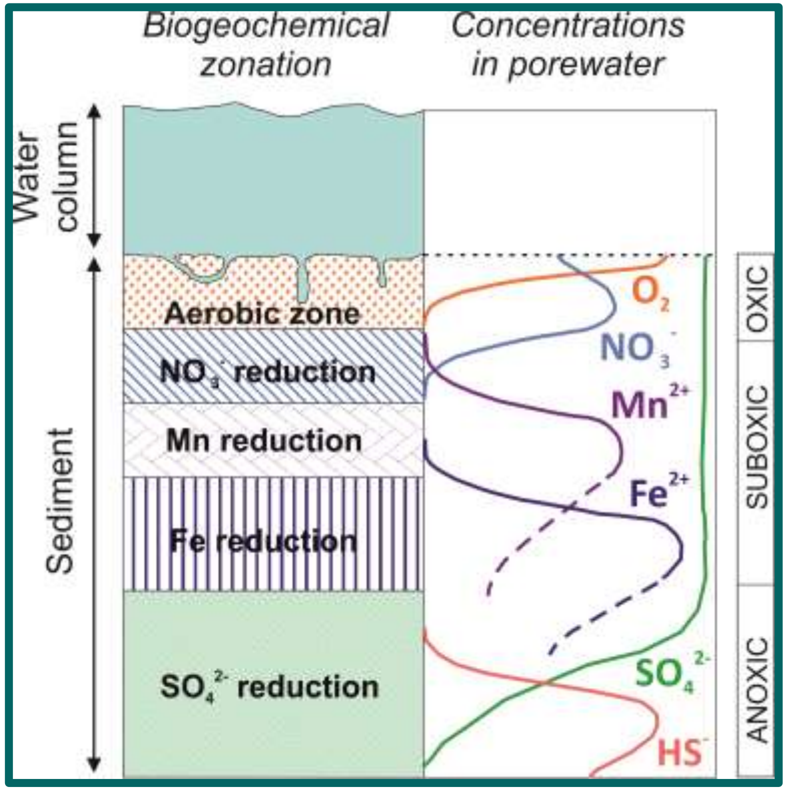
Sediment = sink for contaminants?

Sediment = potential secondary source of contaminants!



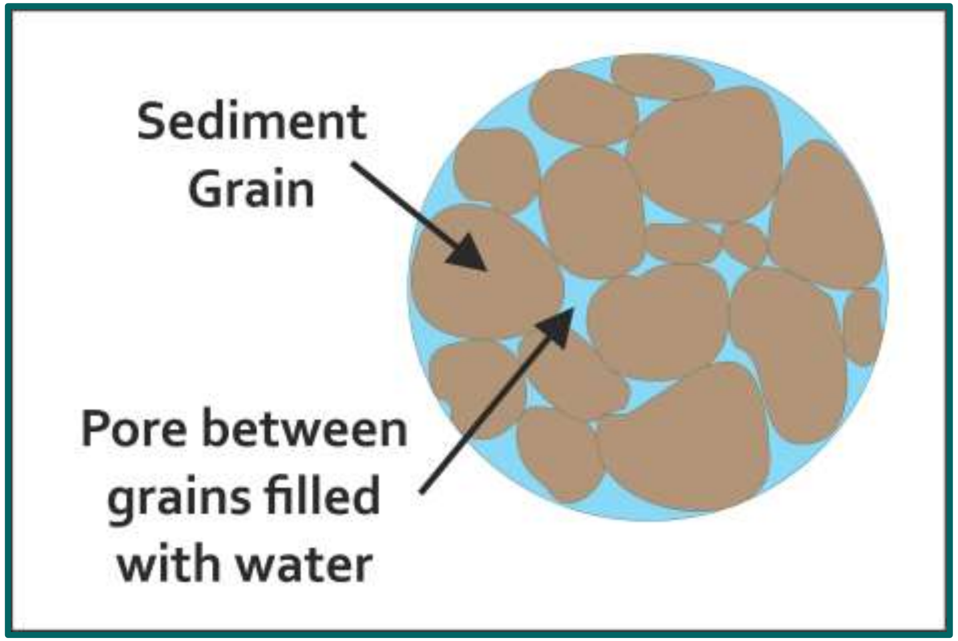
Sediment = sink for contaminants?





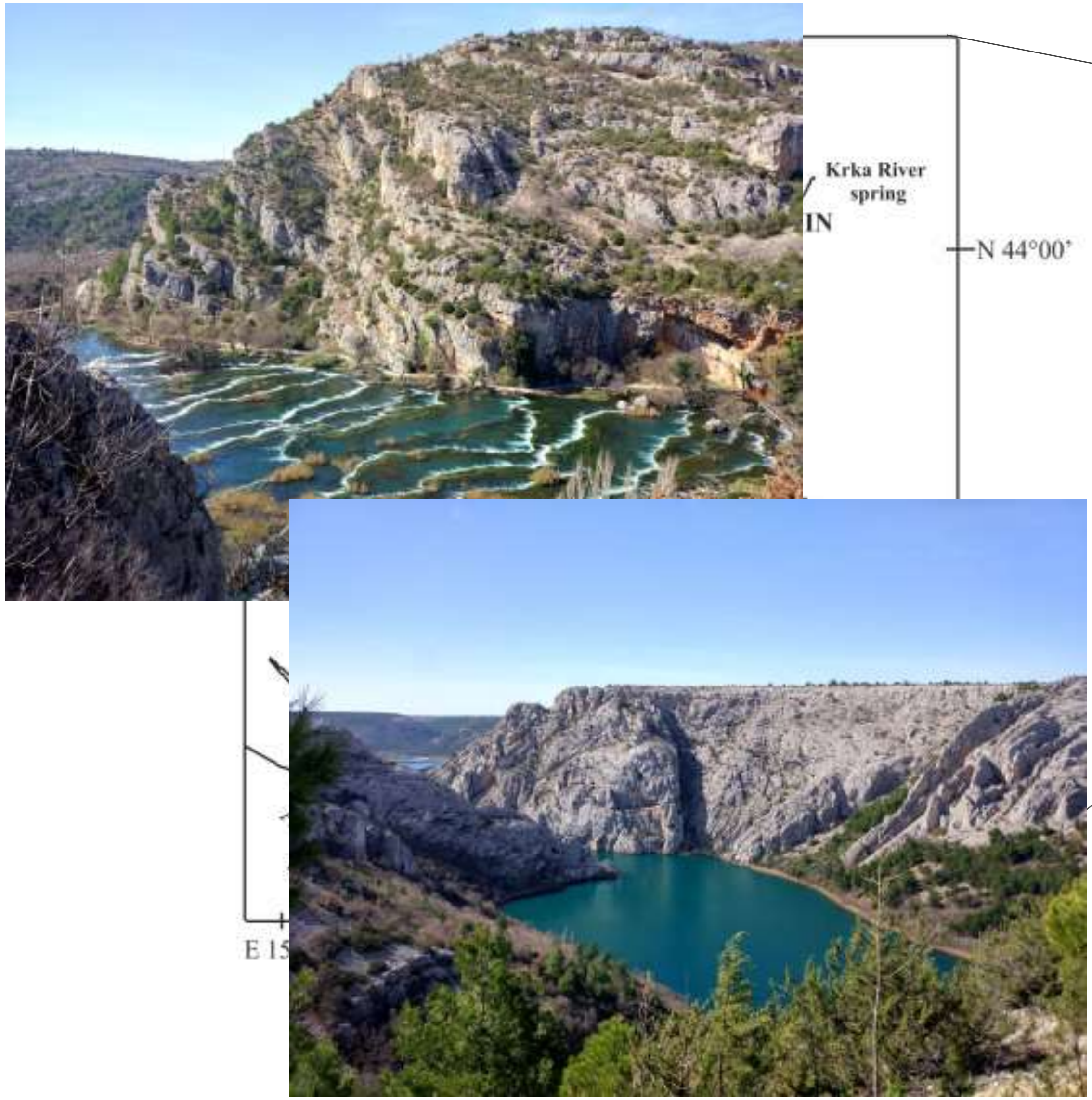
Mineralization of organic matter

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 assessmet and toxicity identification

Study area

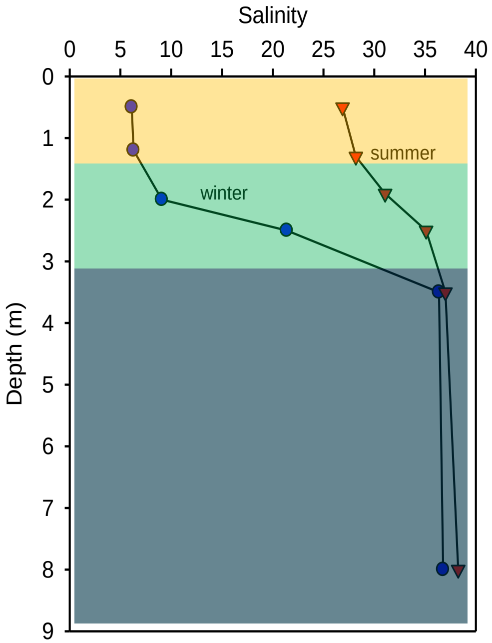


- Krka River – karstic river, eastern coast of the Adriatic Sea (Croatia)
- Krka National Park
- Low input of trace metals, suspended particulate matter and organic carbon by the river.

Krka River estuary

GoogleEarth

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



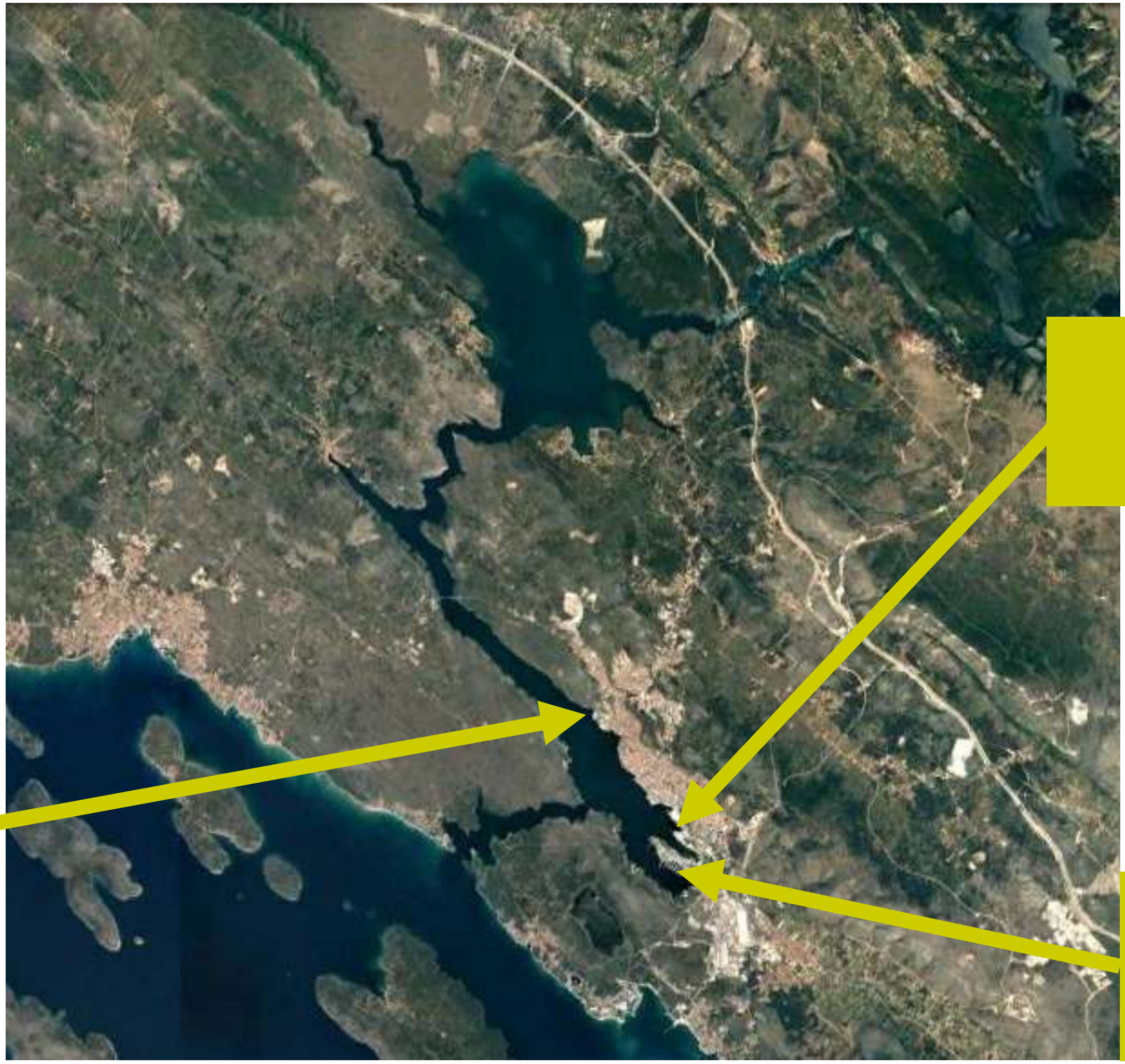
⬅ Brackish layer

⬅ 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

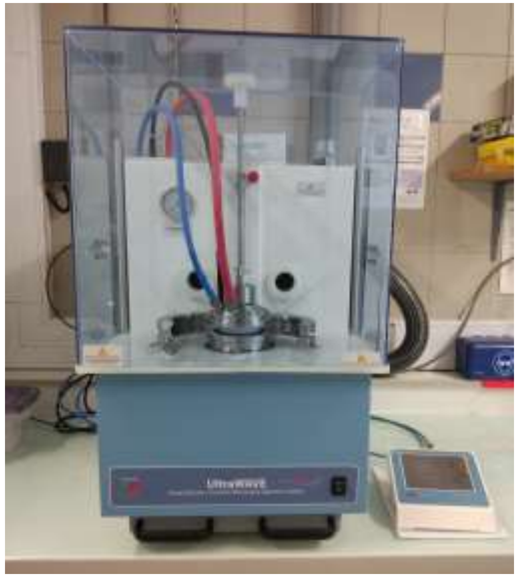
1. Define main source of pollution within the estuary

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

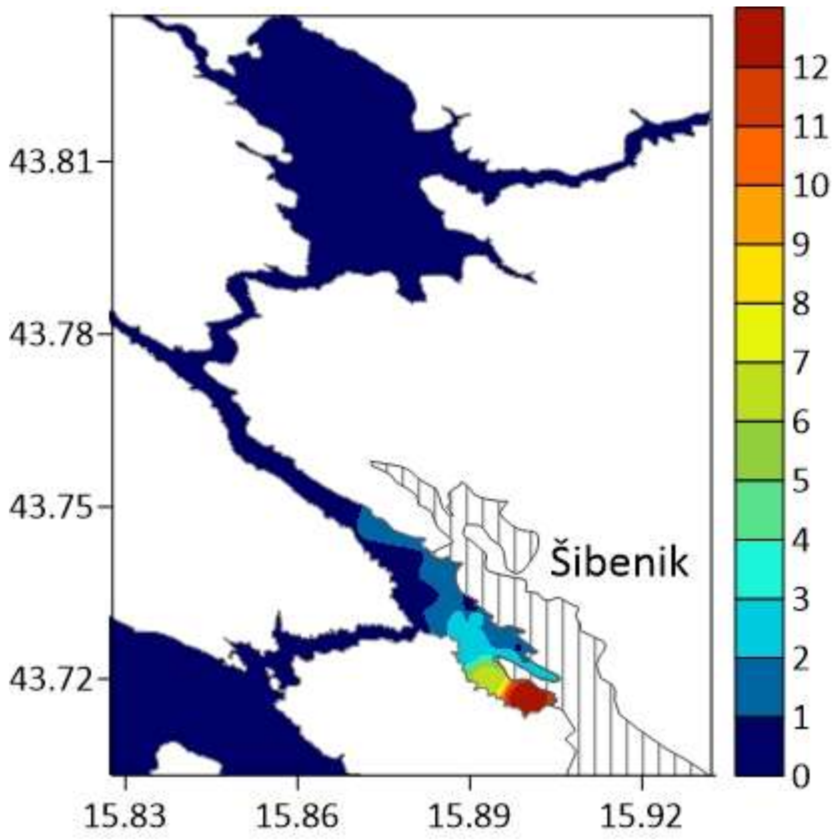
- Sampling - Gravity corer (Uwitec)
- Freezing, lyophilization and sieving <2mm
- Hg - untreated samples - AMA 254 (LECO Corporation)
- Al, As, Ba, Be, Bi, Cr, Cs, Cu, Cd, Co, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, Zn – Aqua Regia digestion - HR ICP-MS (Element 2, Thermo)
- Interpolation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



1st objective
Results

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

Values are expressed in µg g^{-1}



No elevated metal concentrations were found in the upper part of estuary.

1st objective Results

$$Enrichment\ Factor = \frac{\left(\frac{element}{Li}\right) sample}{\left(\frac{element}{Li}\right) background}$$

		Hg	Mn	Cu	Zn	Cd	Pb	As	Cr
EF	min	0.91	0.71	1.11	1.46	0.51	1.18	0.85	0.87
	max	**151**	103	45.4	38.8	36.6	29.6	7.93	3.64
	mean	17.0	5.48	4.98	5.57	2.73	5.37	2.09	1.35

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

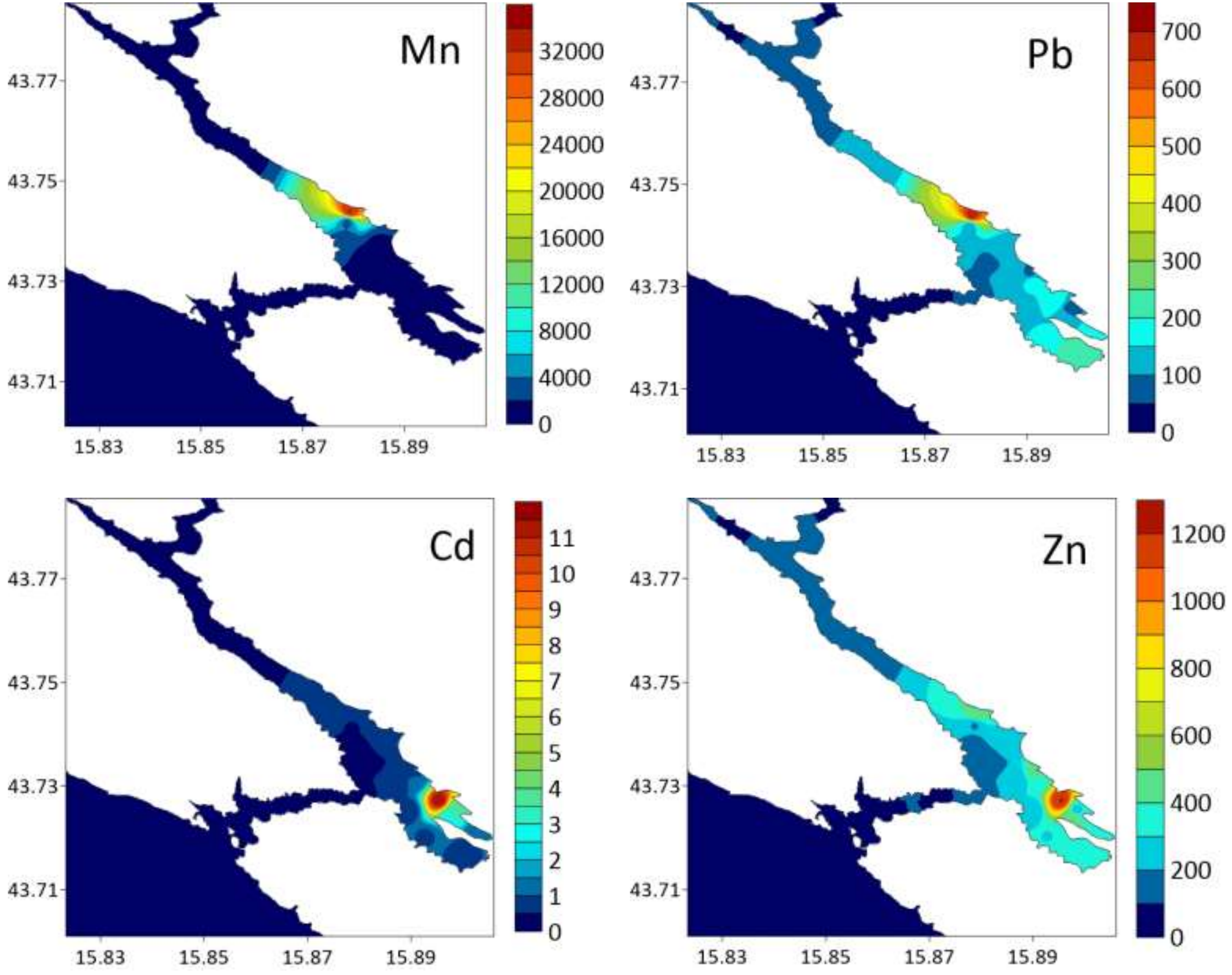
1st objective Results

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)



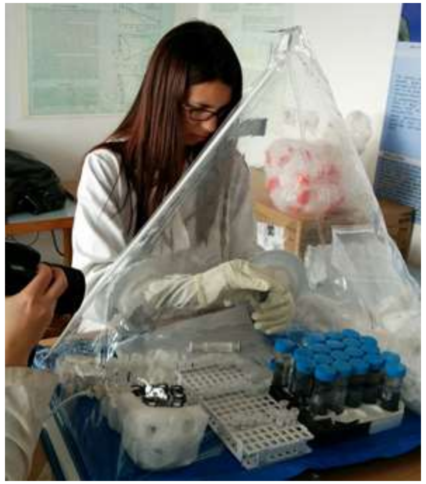
Values are expressed in μg g^{-1}

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



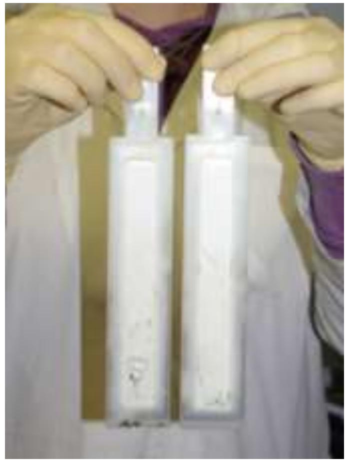




2^{nd} objective - DGT passive samplers

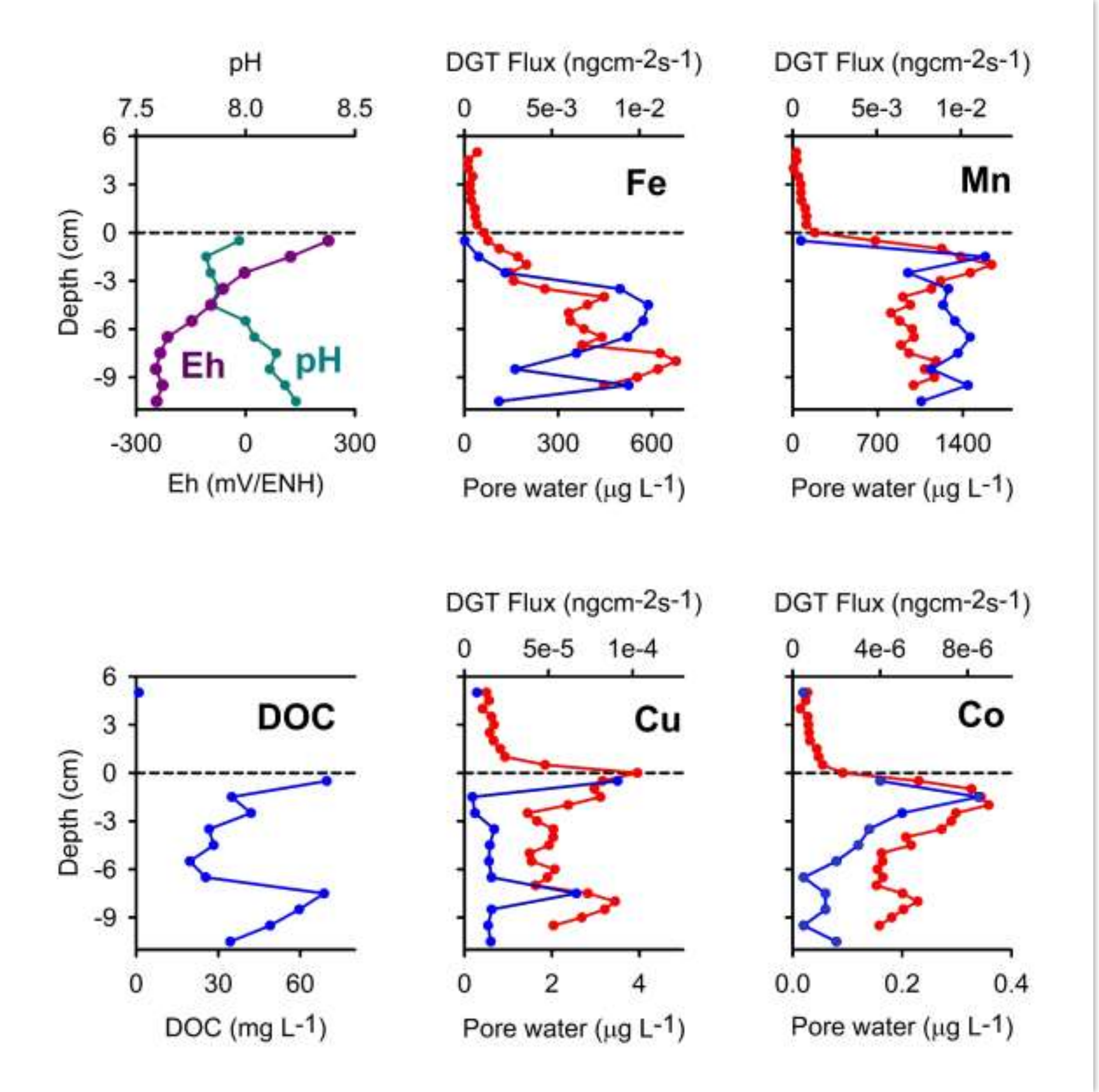
DGT (diffusive gradients in thin films) - simple device uses a layer of binding agent impregnated in a hydrogel to accumulate dissolved substances.

- *in situ* for 94 hours
- resolution of 5 mm
- extraction in 1.5 mL 1M HNO_3
- HR-ICP-MS: Fe, Al, Mn, Ti, Co, Cr, Pb, Ti, Cu, Ni, V, Cd



2nd objective
Results

Processes of early diagenesis control trace metal mobility



DGT
Extracted porewater

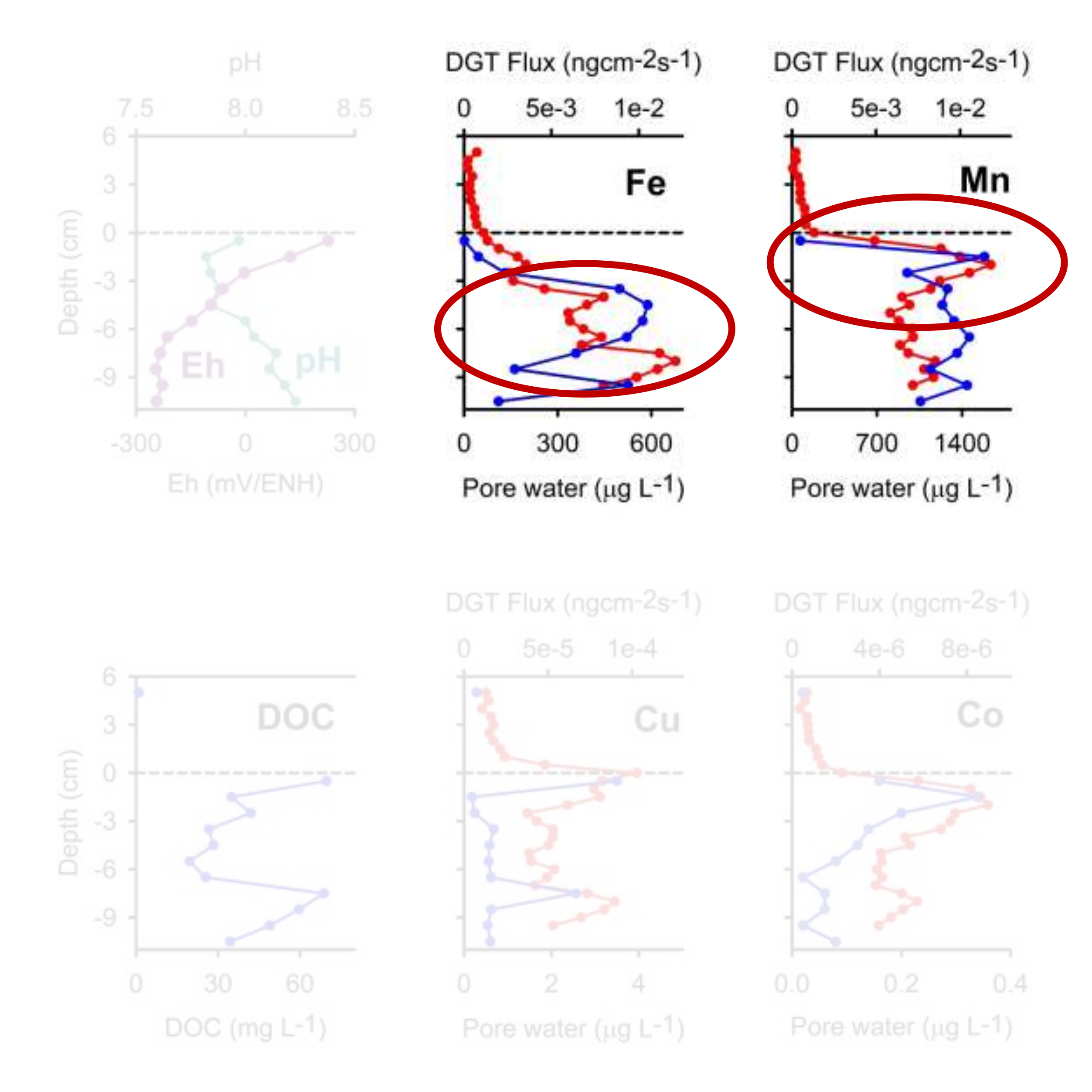
2nd objective Results

Classical diagenetic sequence:

Subsurface peak of Mn (-2 cm), followed by Fe (maximum at -8 cm) related to Mn and Fe oxyhydroxides reduction.

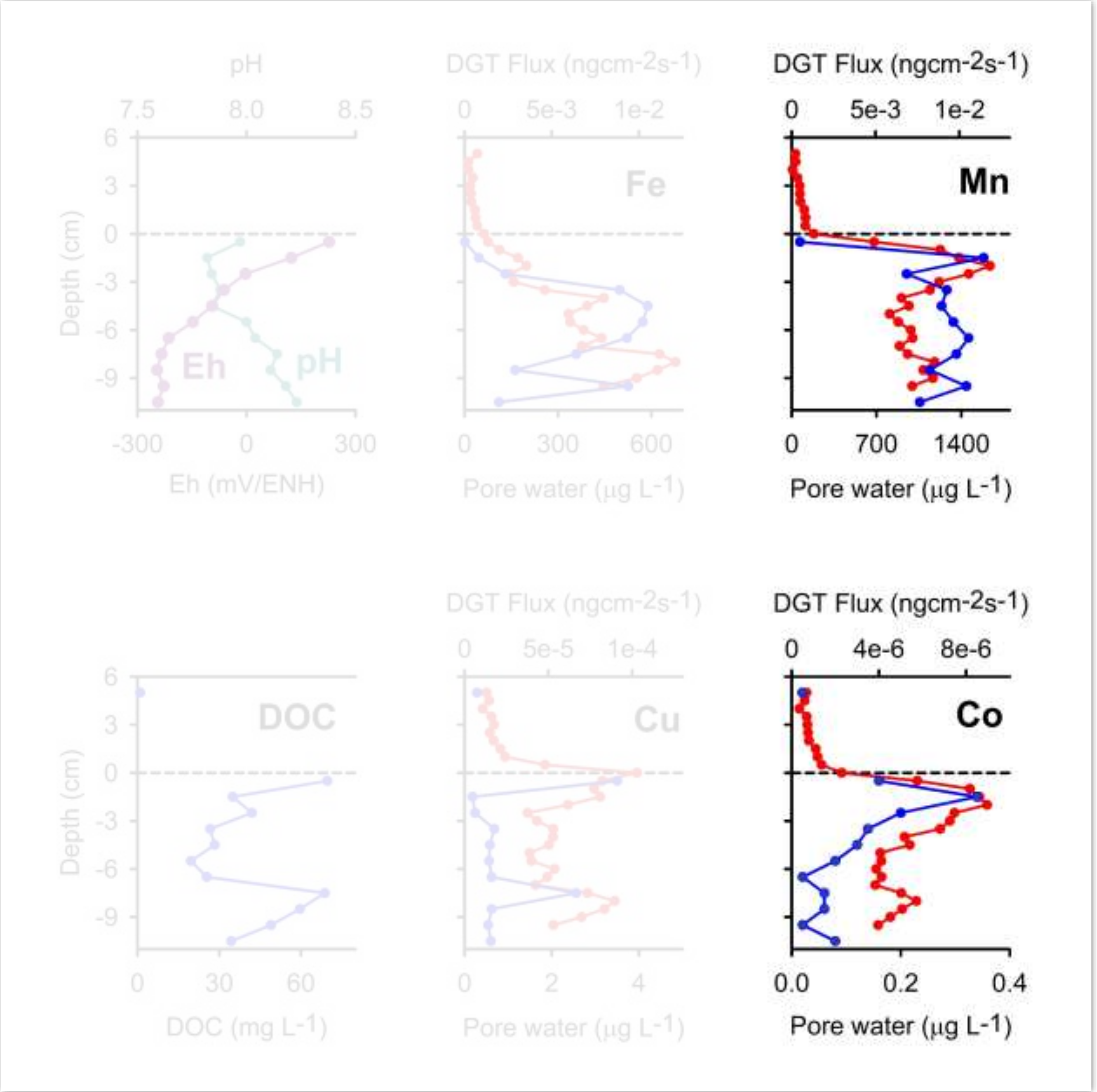
DGT

Extracted porewater



2nd objective Results

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

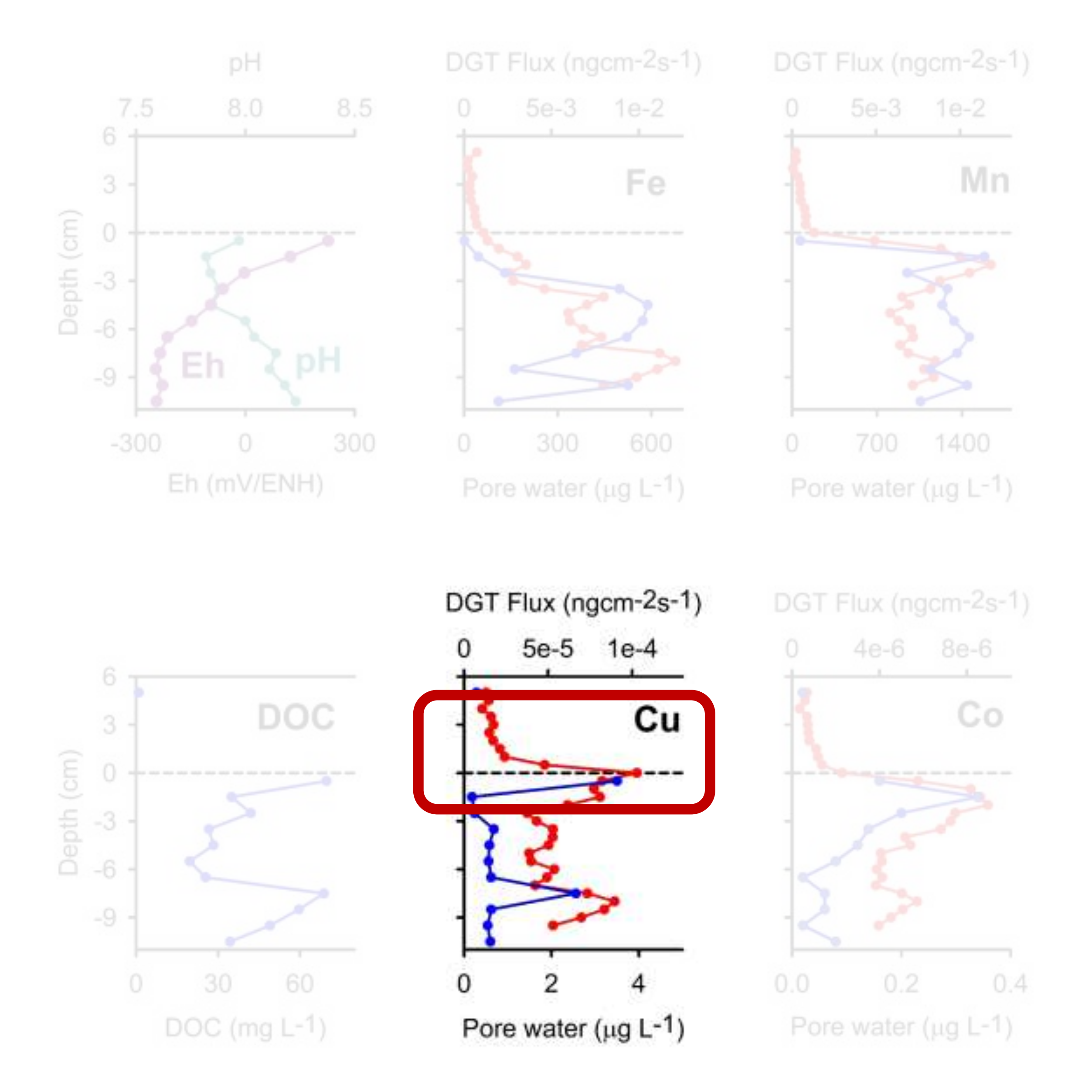


DGT

Extracted porewater

2nd objective Results

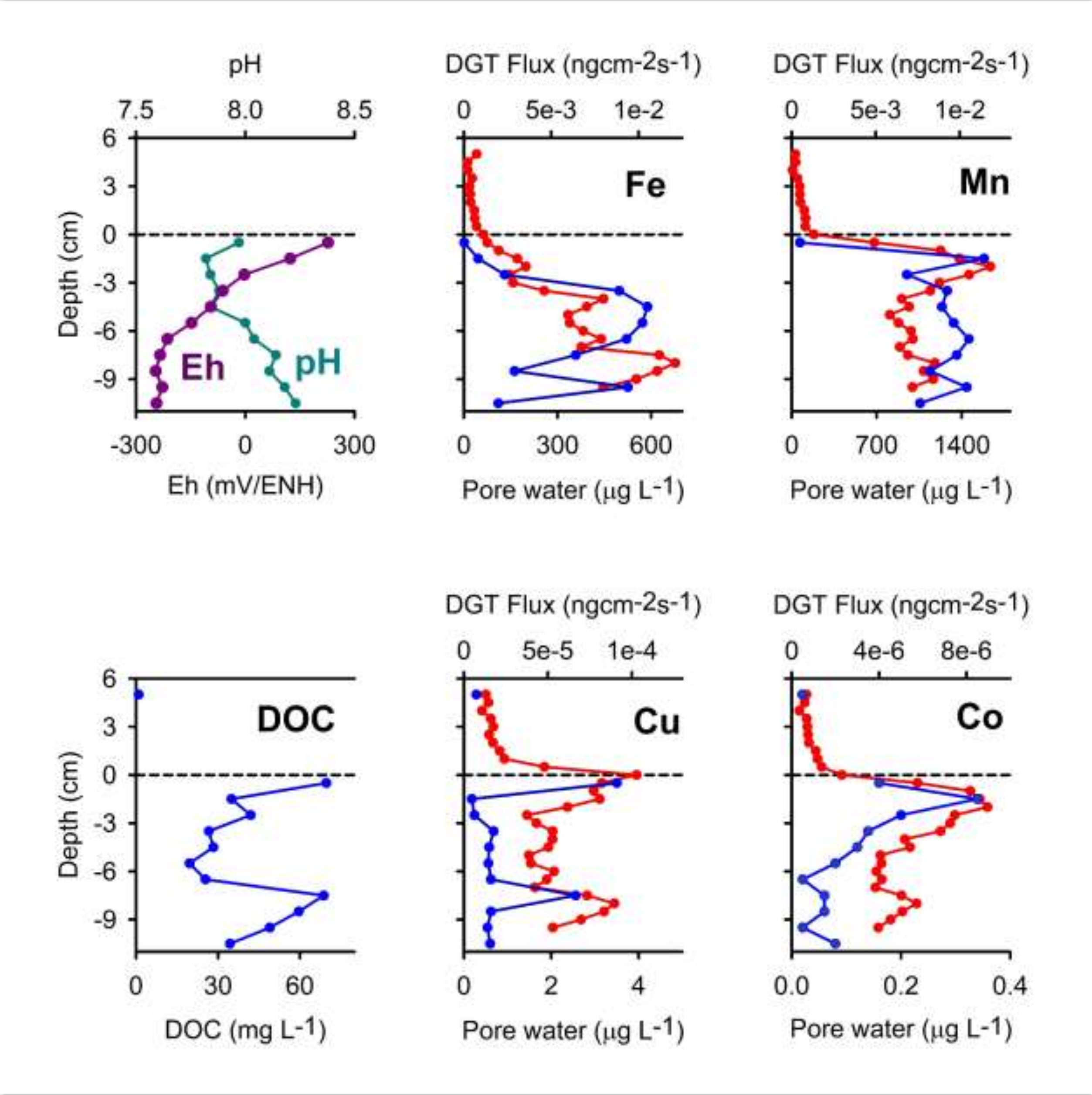
Significant gradient at the sediment/water interface



DGT
Extracted porewater

2nd objective Results

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



DGT
Extracted porewater

Conclusion

Upper part ⟶ low concentrations

Šibenik Bay⟶ anthropogenic pollution

Possible transport to the water column

Thank you!

HrZZ
Hrvatska zaklada
za znanost

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.