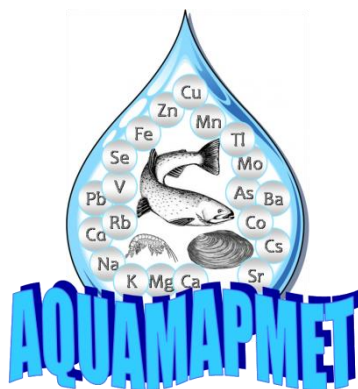


Ruđer Bošković Institute
University of Zagreb, Faculty of Science
University of Pau, France
University of Bordeaux, France

Wrap-up Meeting

December 2 and 3, 2019

Accumulation, Subcellular Mapping and Effects of
Trace Metals in Aquatic Organisms
(AQUAMAPMET)



Aims of the project



- ✓ to increase our understanding and gain new knowledge on how fish, crustaceans, bivalves and fish intestinal parasites (Acantocephalans) cope with elevated metal concentrations in the freshwater ecosystems by relating data on metal concentrations in water, accumulated metals and biomarker responses in biota to data on intracellular metal mapping
- ✓ to evaluate anthropogenic impact on selected freshwater ecosystems referring to metal/metalloid pollution by using integrated chemical, biochemical and biological approach



Specific objectives

Evaluation of metal/metalloid accumulation in fish, acanthocephalans, crustaceans and bivalves

Evaluation of subcellular partitioning of metals/metalloids in fish, acanthocephalans, crustaceans and bivalves

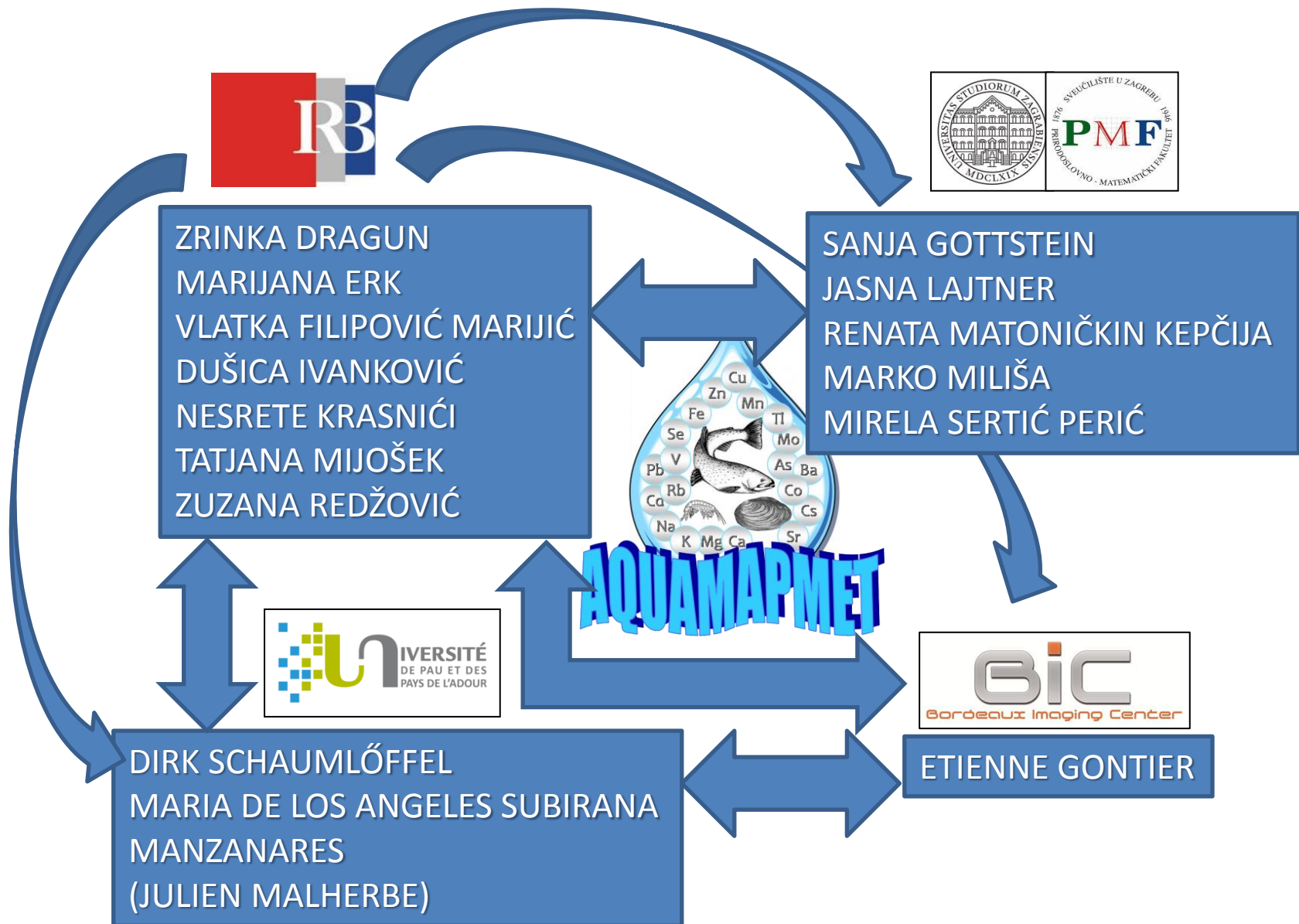
Evaluation of biodiversity of MZB, periphyton and drift

Evaluation of biological effects of contamination on biota

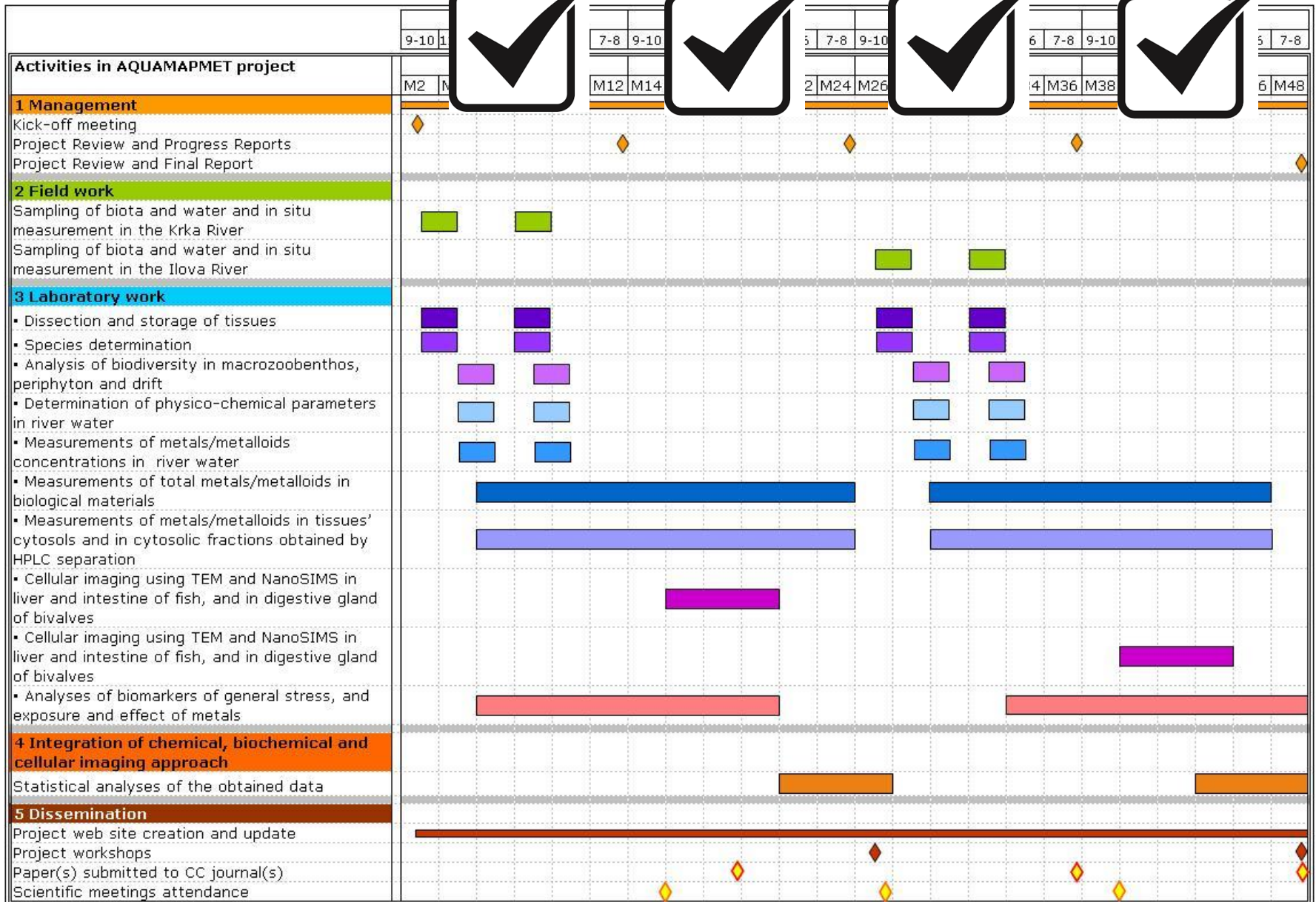
Intracellular mapping of trace metals in fish tissues, acanthocephalans and bivalve tissues, and correlation between two imaging techniques – NanoSIMS and TEM

Integration of chemical, biochemical and cellular imaging approach

Project team



Timing of activities in the AQUAMAPMET project

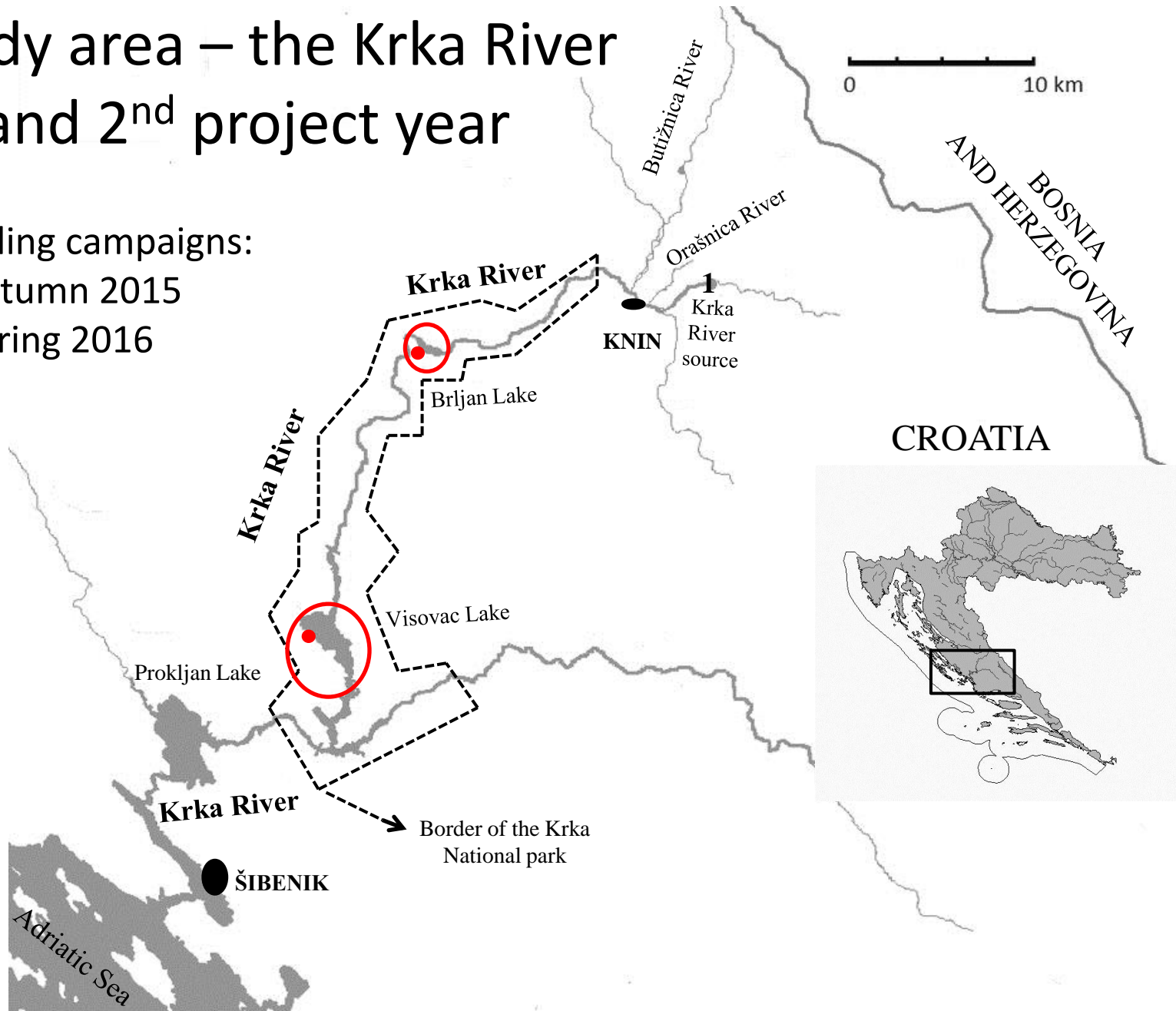


Study area – the Krka River

1st and 2nd project year

Sampling campaigns:

- ✓ autumn 2015
- ✓ spring 2016



The Krka River – sampling locations and field work referent location – Krka River spring



The Krka River – sampling locations and field work industrial area of Knin – river Orašnica



- „Hot-spot” – waste waters not adequately treated nor managed

- the capacity of galvanized zinc plating ~100,000 tons, hot dip galvanizing ~30,000 tons, and heat treatment ~100,000 tons per year



The Krka River – sampling locations and field work downstream from Knin - wastewater discharge



Basic physico-chemical water parameters

- temperature, mean O₂ levels → moderate and uniform
- pH → slightly alkaline environment
- COD and nutrient concentrations → rather low
- site downstream from Knin generally showed higher values of majority of physico-chemical parameters

Limiting values (HR-R_12)

pH 7.0 – 9.0

COD ≤ 4mg O₂ L⁻¹

N-NO₃⁻ ≤ 0.7 mg N L⁻¹

P-PO₄³⁻ ≤ 0.03 mg P L⁻¹

GRC (Government of the Republic of Croatia), 2019. Directive on Water Quality Standard. Official Gazette No.96., Zagreb.

Both studied sampling sites – classified as waters of very good and good water quality

Trace and macro-element concentrations

- significantly higher values at site downstream from Knin: Li, Rb, Mo, Mn, Fe, Sr, and Ca

- significantly higher autumn values were recorded for Se, Rb, Sb, U, Al, Ti, V, Cr, As, Na, Mg and K

- 20% higher levels of Ba, Mo, Ca, Rb
- 2-fold higher levels of Li and Sr
- 17-fold and 38-fold higher levels of Fe and Mn

emerged from municipal and industrial effluents from the town of Knin

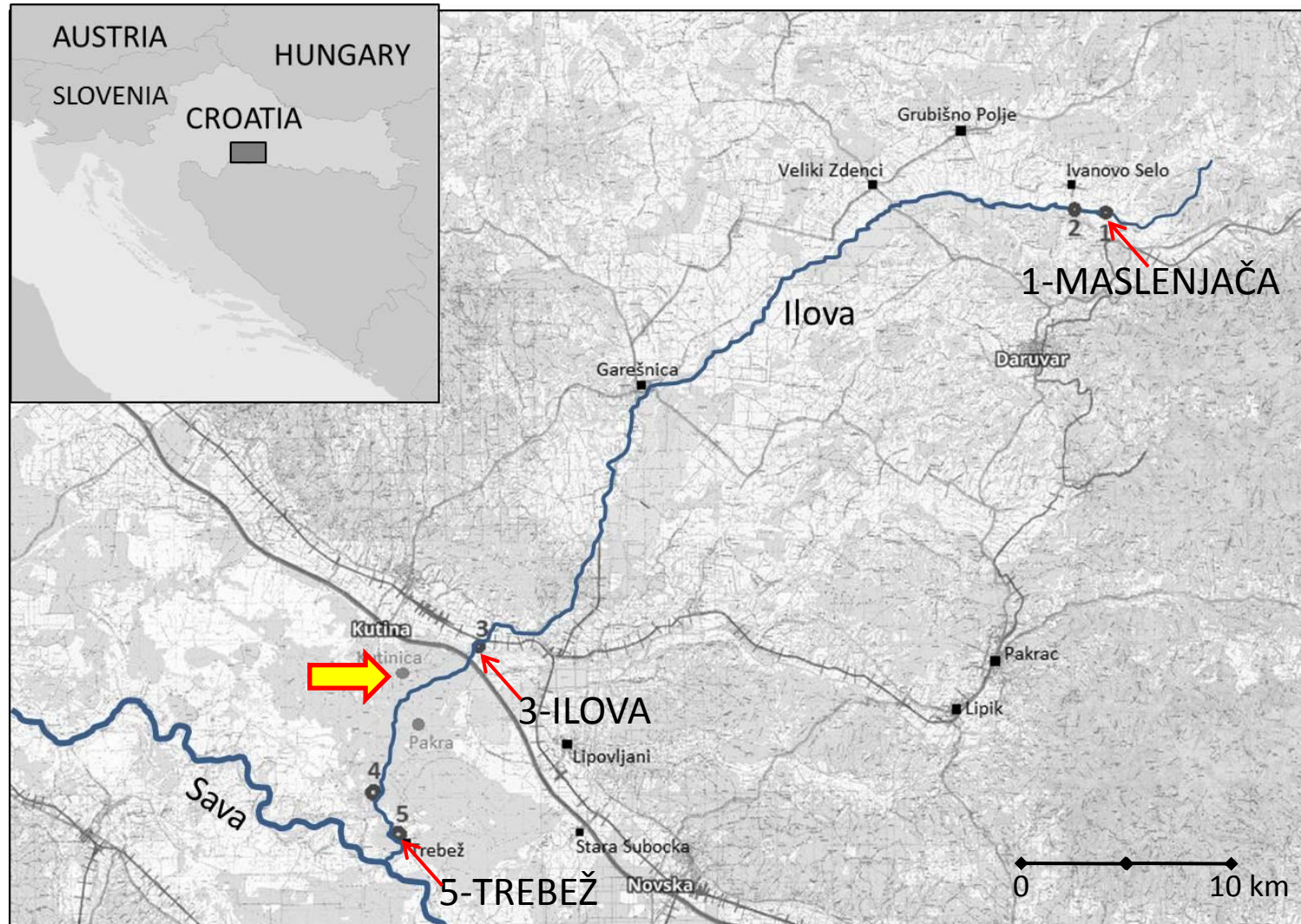
- ✓ both sites in this study could be considered as uncontaminated regarding the metal concentrations
 - ✓ “self-purification ability”

Study area – the Ilova River

3rd and 4th project year

Sampling campaigns:

- ✓ autumn 2017
- ✓ spring 2018

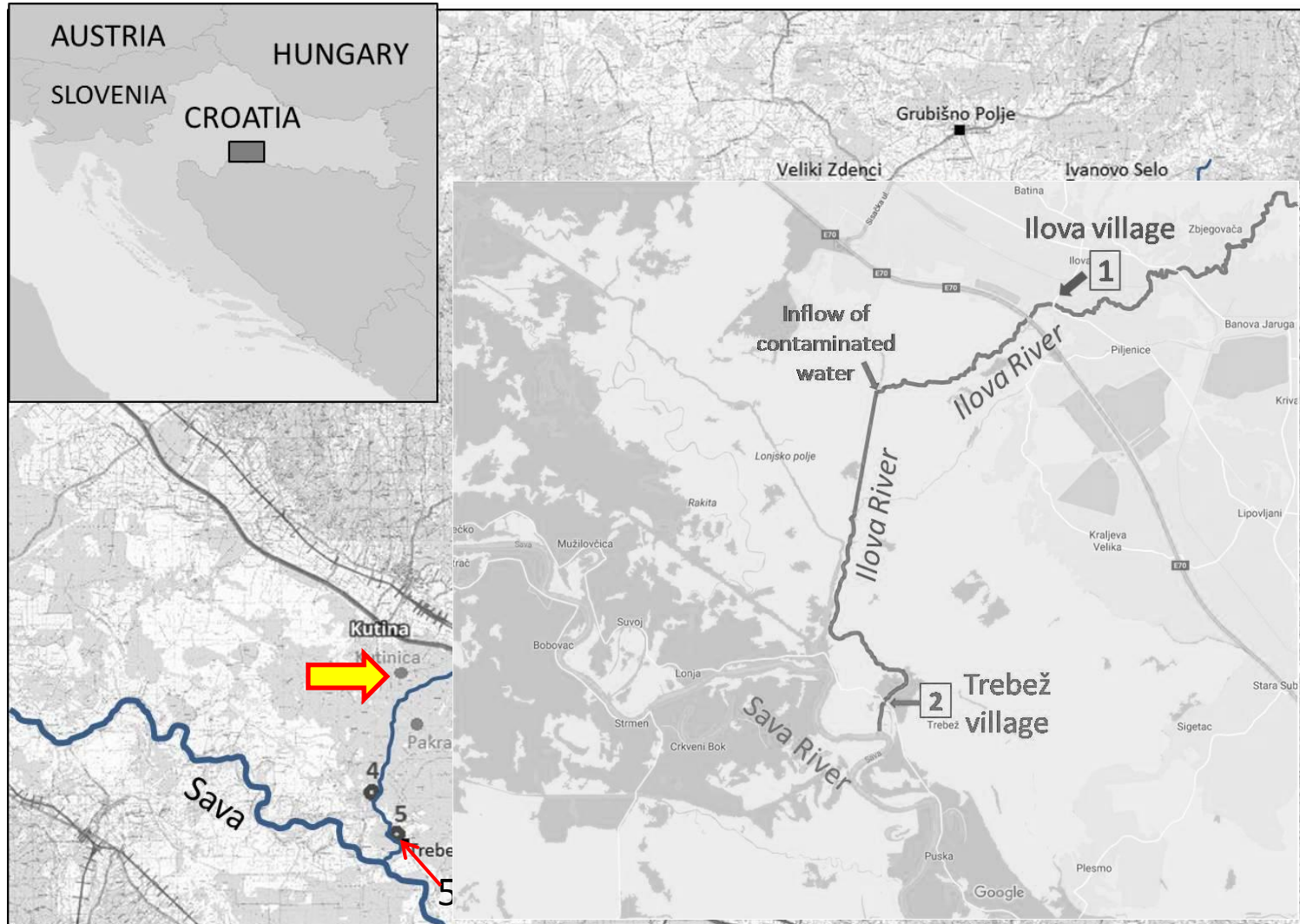


Study area – the Ilova River

3rd and 4th project year

Sampling campaigns:

- ✓ autumn 2017
- ✓ spring 2018



The Ilova River – sampling locations and field work

Village Maslenjača – about 50 km upstream from Kutina



The Ilova River – sampling locations and field work

Village Ilova – upstream from Kutina, about 800 m from highway



The Ilova River – sampling locations and field work

Village Trebež – 15 km downstream from Kutina



Location of anthropogenic influence



Kutinica - before the confluence into Ilova



Phosphogypsum storage ponds

Phosphogypsum → a waste by-product from the processing of phosphate rock in factories producing phosphoric acid and phosphate fertilizers

The filter-cake is slurried with the water and pumped to special storage ponds where the solid part is settled and covered with highly acidic transport water (pH 2–3) containing high concentrations of fluoride and elevated amounts of heavy metals.



Photo: Google Earth

Phosphogypsum storage ponds

IMPURITIES: radionuclides, and trace metals like As, Pb, Cd, Cr, Mn, Fe, Ni, Cu, Zn, Sb, V

Basic physico-chemical water parameters

Site no.	Location	O ₂ (mg L ⁻¹)	O ₂ %	pH	Conductivity (μS cm ⁻¹)	COD _{KMnO4} (mg O ₂ L ⁻¹)	N-NO ₃ ⁻ (mg L ⁻¹)	P-PO ₄ ³⁻ (mg L ⁻¹)
1	Maslenjača	8.5	86	8.03	332	3.9	1.13	0.10
3	Ilova	8.2	82	7.55	328	9.0	2.89	0.7
5	Trebež	5.0	52	7.39	473	6.8	4.54	0.23 (937)
	Kutinica	2.8	36	7.63	753	6.7	2.14- 11,688	0.56

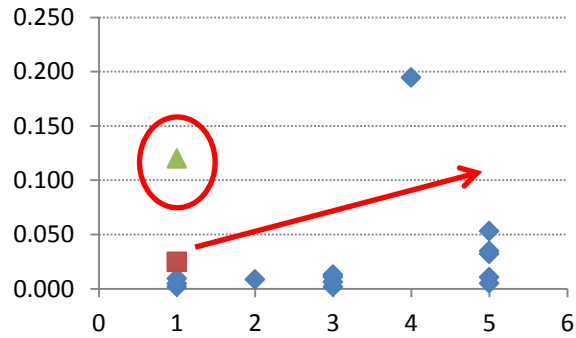
Maslenjača → only one of all studied sampling sites – classified as good water quality

Limiting values (HR-R₄):
 pH 7.0 – 9.0
 COD ≤ 5.5 mg O₂ L⁻¹
 N-NO₃⁻ ≤ 1.3 mg N L⁻¹
 P-PO₄³⁻ ≤ 0.1 mg P L⁻¹

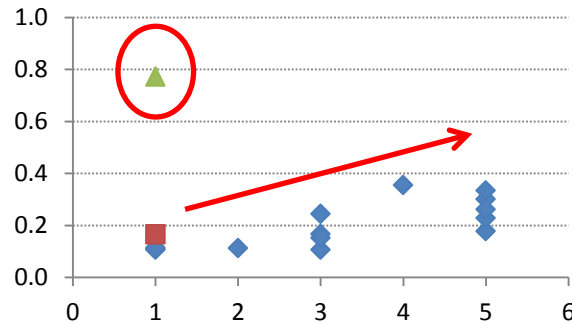
Directive on Water Quality Standard.
 Official Gazette No.96(2019), Zagreb.

Dissolved trace elements in water of Ilova

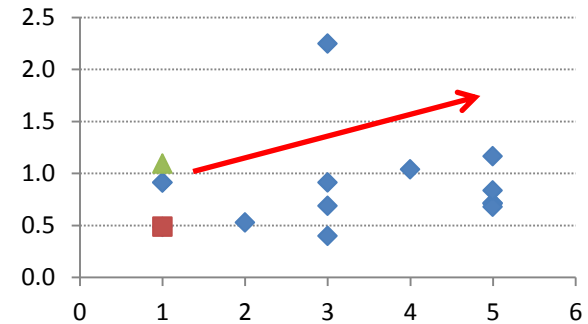
Cadmium ($\mu\text{g L}^{-1}$)



Antimony ($\mu\text{g L}^{-1}$)

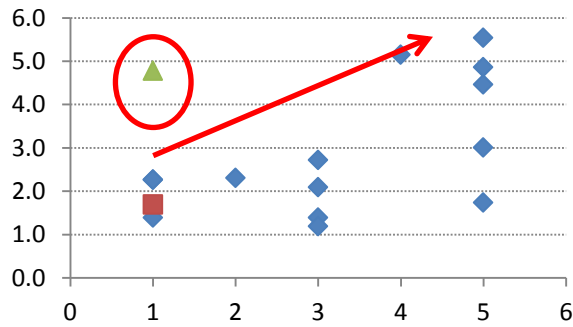


Copper ($\mu\text{g L}^{-1}$)

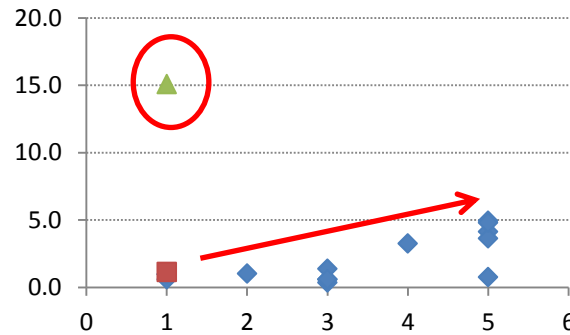


◆ Ilova
■ Pakra
▲ Kutinica

Arsenic ($\mu\text{g L}^{-1}$)

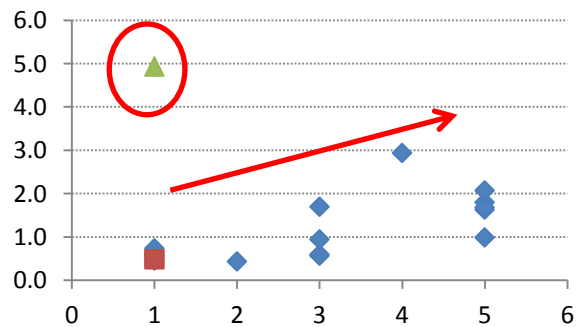


Vanadium ($\mu\text{g L}^{-1}$)

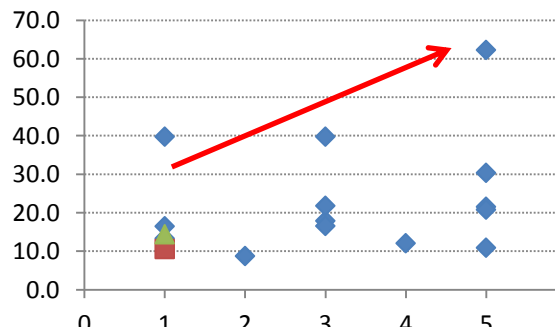


◆ Ilova
■ Pakra
▲ Kutinica

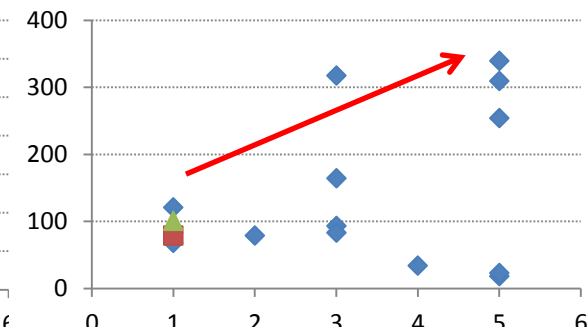
Nickel ($\mu\text{g L}^{-1}$)



Iron ($\mu\text{g L}^{-1}$)

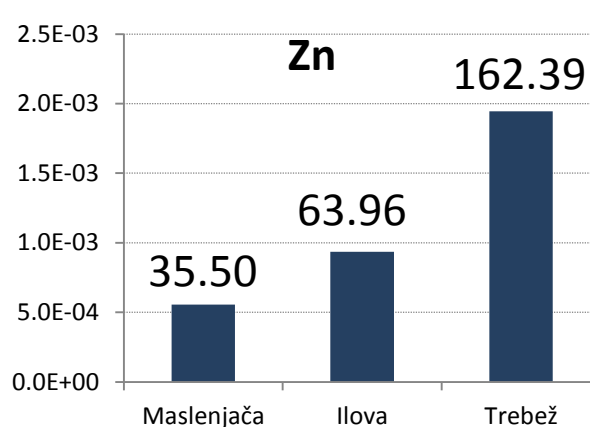
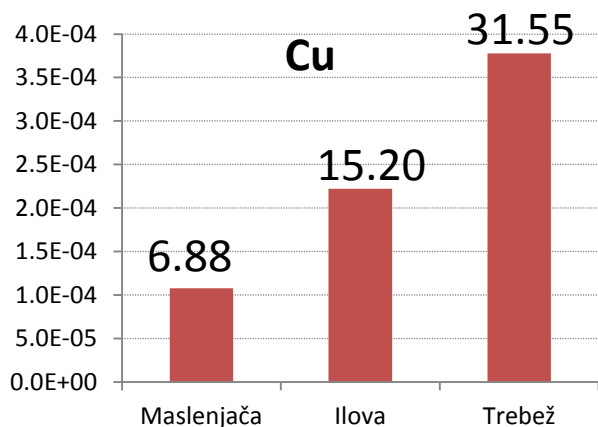
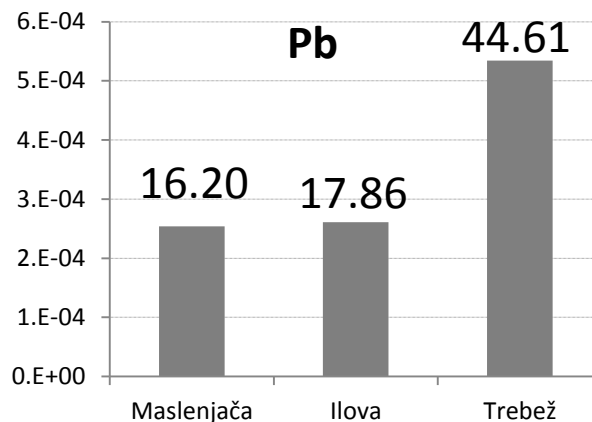
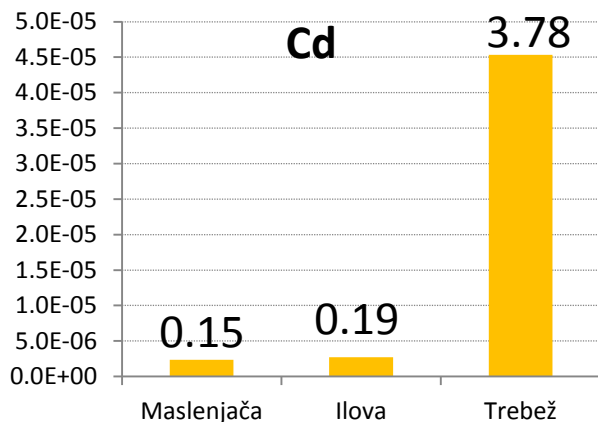


Manganese ($\mu\text{g L}^{-1}$)



◆ Ilova
■ Pakra
▲ Kutinica

Trace elements (normalized to Al) in surface sediments of Ilova



• Increasing concentration gradient in downstream direction

↓

ANTROPOGENIC IMPACT

Concentration in mg/kg (dry sediment)

Published results

Croatian scientific

BIBLIOGRAPHY



<http://bib.irb.hr/lista-radova?&lang=EN>

Browsing

Project number: HRZZ-IP-2014-09-4255

Journal articles and review articles in CC journals:	8
Scientific papers in other journals:	1
Conference reports (abstracts) in CC journals:	1
Conference reports (abstracts) in other journals:	2
Papers in the publishing process:	1
Other refereed conference papers:	1
Abstracts in Book of abstracts:	23
Graduation thesis:	2+1
Rector's award paper:	1



Contents lists available at ScienceDirect
Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Benthos-drift relationships as proxies for the detection of the most suitable bioindicator taxa in flowing waters – a pilot-study within a Mediterranean karst river



Mirela Sertić Perić^{a,*}, Renata Matoničkin Kepčija^a, Marko Miliša^a, Sanja Gottstein^a, Jasna Lajtner^a, Zrinka Dragun^b, Vlatka Filipović Marijić^b, Nesrete Krasnići^b, Dušica Ivanković^b, Marijana Erk^c

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Science of the Total Environment 642 (2018) 656–664



Contents lists available at ScienceDirect
Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



Evaluation of architectural and histopathological biomarkers in the intestine of brown trout (*Salmo trutta* Linnaeus, 1758) challenged with environmental pollution



Josip Barišić^a, Vlatka Filipović Marijić^{b,*}, Tatjana Mijošek^b, Rozelindra Čož-Rakovac^a, Zrinka Dragun^b, Nesrete Krasnići^b, Dušica Ivanković^b, Dáša Kružlicová^c, Marijana Erk^b

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^c University of SS Cyril and Methodius, Faculty of Natural Sciences, Department of Chemistry, Nám. J. Herdu 2, 949 01 Trnava, Slovakia

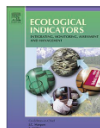
Ecological Indicators 105 (2019) 188–198



Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind



Comparison of electrochemically determined metallothionein concentrations in wild freshwater salmon fish and gammarids and their relation to total and cytosolic metal levels



Tatjana Mijošek^{a,*}, Vlatka Filipović Marijić^a, Zrinka Dragun^a, Dušica Ivanković^a, Nesrete Krasnići^a, Marijana Erk^a, Sanja Gottstein^b, Jasna Lajtner^b, Mirela Sertić Perić^b, Renata Matoničkin Kepčija^b

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^b University of Zagreb, Faculty of Science, Department of Biology, Division of Zoology, Rooseveltov trg 6, 10000 Zagreb, Croatia



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Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Total and cytosolic concentrations of twenty metals/metalloids in the liver of brown trout *Salmo trutta* (Linnaeus, 1758) from the karstic Croatian river Krka



Zrinka Dragun^{a,*}, Vlatka Filipović Marijić^a, Nesrete Krasnići^a, Dušica Ivanković^a, Damir Valić^b, Jakov Žunić^b, Damir Kapetanović^b, Irena Vardić Smrzlić^b, Zuzana Redžović^c, Ivana Grgić^c, Marijana Erk^a

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Chemosphere 207 (2018) 162–173



Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere



Cytosolic distributions of highly toxic metals Cd and Tl and several essential elements in the liver of brown trout (*Salmo trutta* L.) analyzed by size exclusion chromatography and inductively coupled plasma mass spectrometry



Zrinka Dragun^{a,*}, Nesrete Krasnići^a, Nicol Kolar^b, Vlatka Filipović Marijić^a, Dušica Ivanković^a, Marijana Erk^a

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^b University of Zagreb, Faculty of Science, Department of Biology, Rooseveltov trg 6, 10000, Zagreb, Croatia



Evaluation of multi-biomarker response in fish intestine as an initial indication of anthropogenic impact in the aquatic karst environment

Tatjana Mijošek*, Vlatka Filipović Marijić, Zrinka Dragun, Nesrete Krasnići, Dušica Ivanković, Marijana Erk

Ruder Bošković Institute, Division for Marine and Environmental Research, Laboratory for Biological Effects of Metals, Bijenička c. 54, 10000 Zagreb, Croatia

CSIRO PUBLISHING

Environ. Chem.

<https://doi.org/10.1017/EN19165>

SPECIAL ISSUE

Research Paper

Thallium accumulation in different organisms from karst and lowland rivers of Croatia under wastewater impact

Tatjana Mijošek,^{1,2,3} Vlatka Filipović Marijić,⁴ Zrinka Dragun,⁴ Dušica Ivanković,⁴ Nesrete Krasnići,⁴ Zuzana Redžović,⁴ Marina Veseli,⁵ Sanja Gottstein,⁶ Jasna Lajtner,⁶ Mirela Šertić Perić,⁶ Renata Matoničkin Kepčija⁶ and Marijana Erk⁴

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Electrochemical Determination of Metallothioneins by the Modified Brdička Procedure as an Analytical Tool in Biomonitoring Studies

Tatjana Mijošek*, Marijana Erk, Vlatka Filipović Marijić, Nesrete Krasnići, Zrinka Dragun, Dušica Ivanković

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Metallomics

PAPER

View Article Online
View Journal



Cite this: DOI: 10.1039/c9mt00036d

Characterization and identification of selected metal-binding biomolecules from hepatic and gill cytosols of Vardar chub (*Squalius vardarensis* Karaman, 1928) using various techniques of liquid chromatography and mass spectrometry†

Nesrete Krasnići,^a Zrinka Dragun,^{1,2,3} Snježana Kazazić,^b Hasan Muharemović,^b Marijana Erk,^a Maja Jordanova,^c Katerina Rebok^c and Vasil Kostov^d

Young researchers – short-term research visits, workshops, courses, trainings...







Thank you!