Metal/metalloid concentrations in water and biota: long-term trends of metal concentrations and water quality of the wastewater impacted Krka River course

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KICK-OFF MEETING

Integrated evaluation of aquatic organism responses to metal exposure: gene expression, bioavailability, toxicity and biomarker responses (BIOTOXMET)

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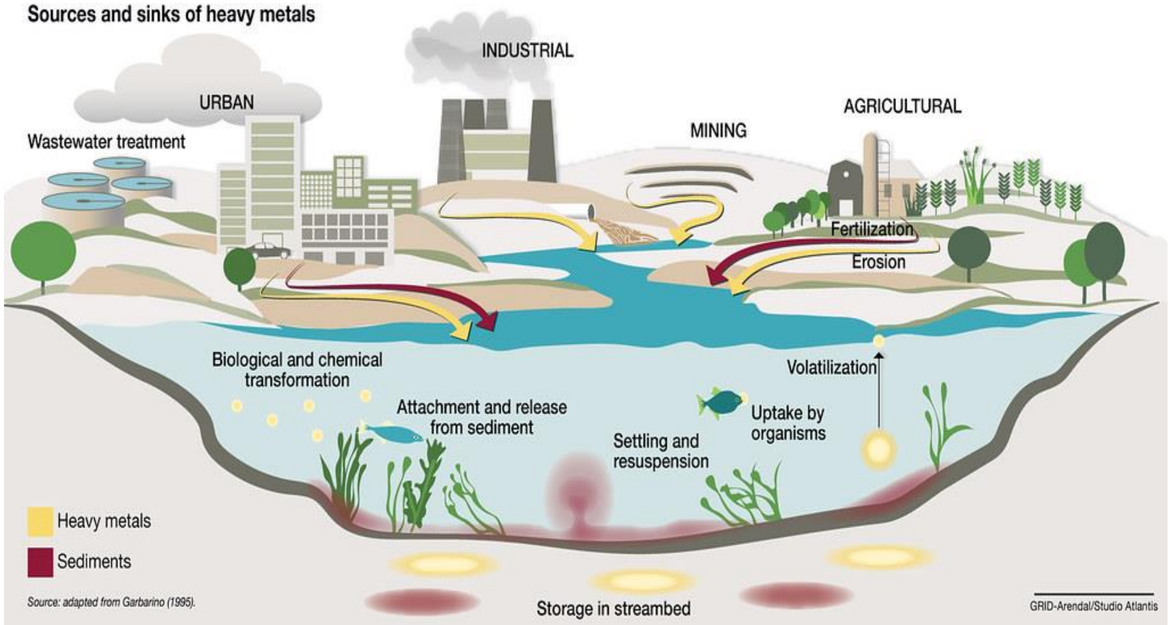
Metals in aquatic ecosystems

✓ **Natural**

- erosion
- volcanic activities
- forest fires and biogenic source
- particles released by vegetation
- atmospheric deposition
- weathering of minerals

✓ **Anthropogenic**



- **Metals are not biodegradable and can acumulate in the sediments and organisms or stay in the water column**
- represent a serious threat to the aquatic environments and living organisms due to their toxicity and persistance

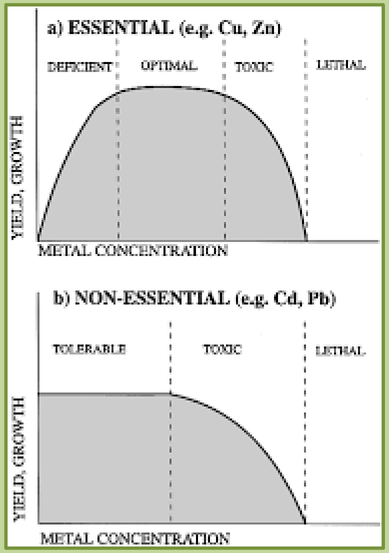
Metals in biota

Essential metals

Na, K, Mg, Ca, Cu, Zn, Fe, Mn

Nonessential metals

Cd, Hg, Ag, Pb



• Sites of metal uptake in the aquatic organisms - **integument, gills, the intestine or the combination of all of these ways**

• Indicator organs – **metabolically active tissues (liver, kidney), the uptake sites for toxicants (gills, intestinal tissue)**

dietborne metal uptake may be of equal or greater importance than the waterborne, but still rarely used in research

Bioindicator organisms in BIOTOXMET

Salmo trutta **Linnaeus, 1758**

Soft tissues

Intestine

Differential centrifugation

a) **metal sensitive fraction (MSF)** including organelles and heat-denaturated proteins (HDP)

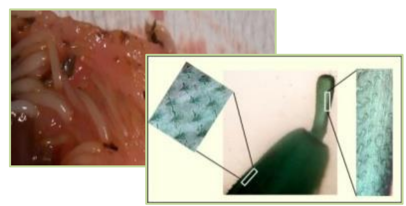
b) **biologically detoxified metals (BDMs)** that are bound to **metal-rich granules (MRG)** and **heat-stable proteins (HSPs)**

c) **trophically available metals (TAM)** which include all fractions except MRG, actually the ones that are bioavailable to predators

Muscle

Edible part

acanthocephalans



Dentitruncus truttae

Sinzar, 1955

efficient metal accumulation

mechanism of metal uptake and binding in acanthocephalans is unknown?

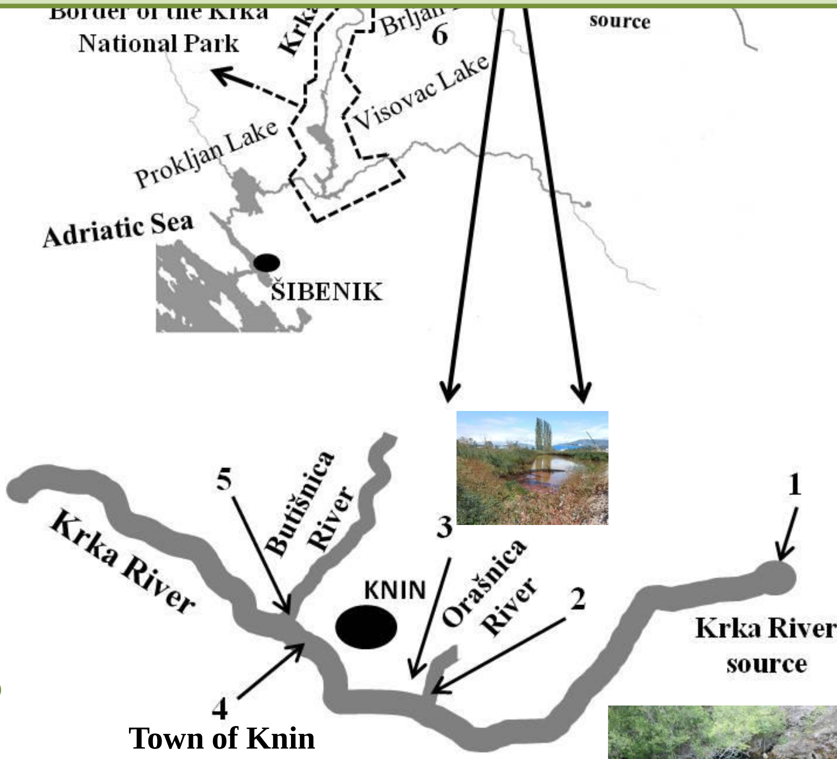
Calcified structures

otoliths

scales

Metal distribution within subcellular fractions of fish intestine will upgrade the knowledge on dietborne metal uptake and possible metal toxicity

Continuation of the previous projects (2015-2016) ⟶ Krka River source (KRS) was selected as the reference, while other locations were under different anthropogenic impact: wastewater from the screw factory (IWW), tributary Orašnica (TOR) passing nearby wastewater basins, Krka River downstream of the municipal sewage of the Town of Knin (KRK), tributary Butišnica (TBU) affected by agricultural activity and Brljan Lake (KBL) as downstream location in Krka NP ⟶ water quality assessment by measuring physico-chemical parameters and dissolved metals concentrations in water.



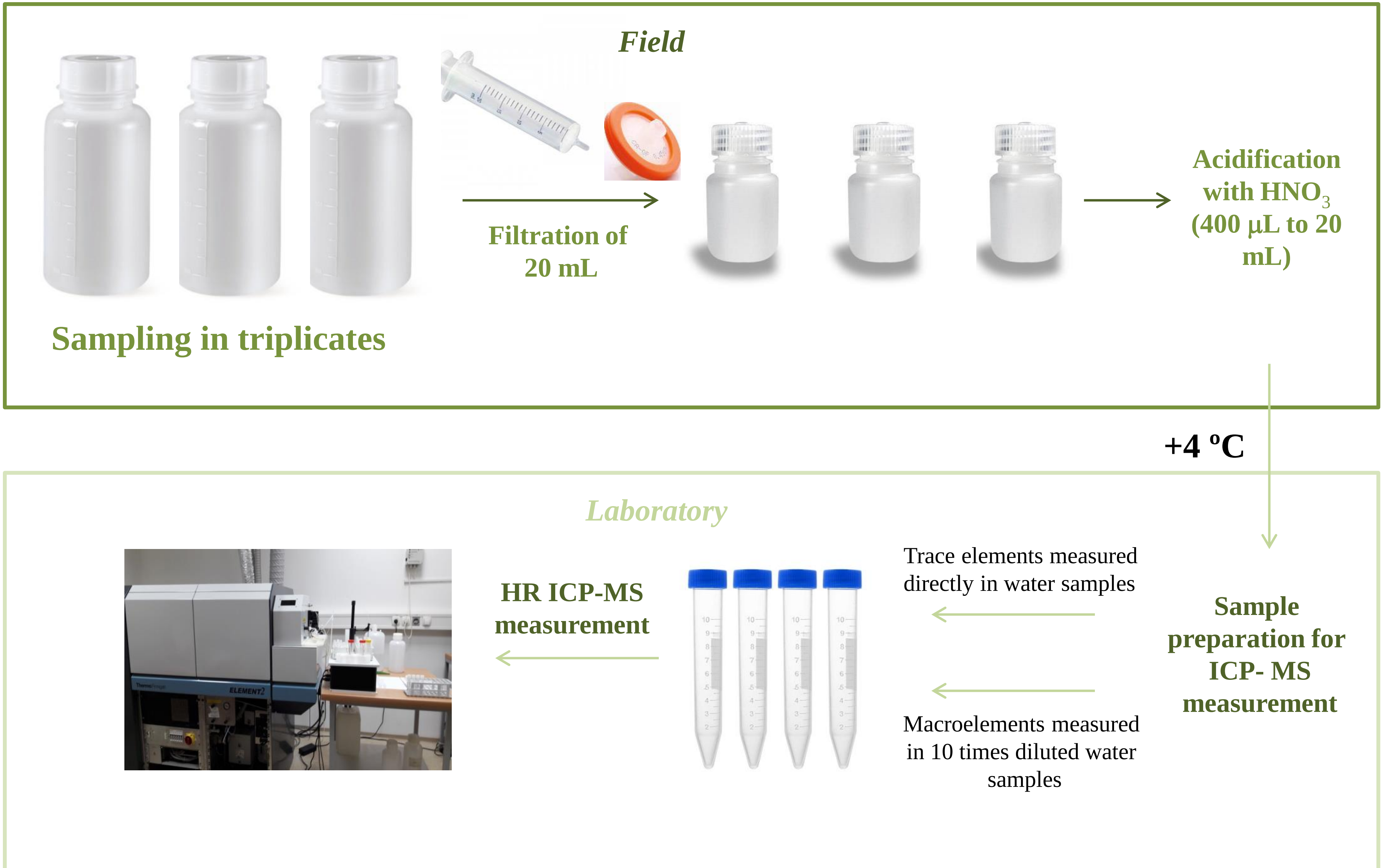
Sampling campaigns:

- ✓autumn 2015
- ✓spring 2016
- ✓ winter 2021

Locations:

- ✓1 Krka River source – KRS
- ✓2 Orašnica River – TOR
- ✓3 Industrial wastewaters - IWW
- ✓4 Town of Knin – KRK
- ✓5 Butišnica River – TBU
- ✓6 Brljan Lake - KBL

Methods



Field
Sampling in triplicates
Filtration of 20 mL
Acidification with HNO_3 (400 μL to 20 mL)
+4 °C
Laboratory
Sample preparation for ICP- MS measurement
Trace elements measured directly in water samples
Macroelements measured in 10 times diluted water samples
HR ICP-MS measurement

Results

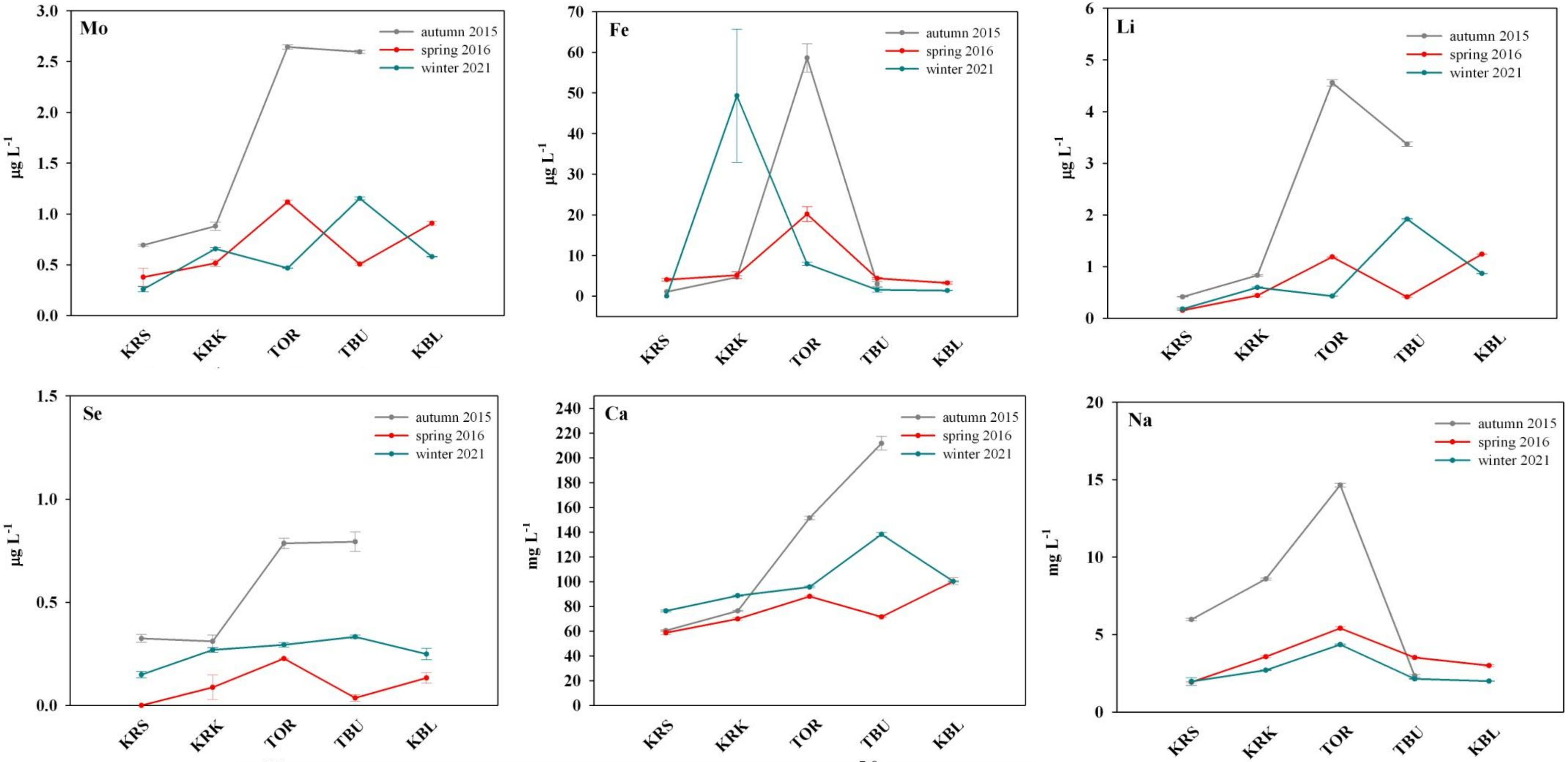
Physico-chemical parameters

- temperature, O_2 levels → mostly moderate and uniform
- pH → slightly alkaline environment

Limiting values (HR-R_12)
pH 7.0 – 9.0
Total ammonium ≤ 0.05 mg N L^{-1}
Total nitrogen ≤ 1 mg N L^{-1}
Total phosphorus ≤ 0.06 mg P L^{-1}
N-NO_3^- ≤ 0.7 mg N L^{-1}
P-PO_4^{3-} ≤ 0.03 mg P L^{-1}

	KRS			KRK			TOR			TBU		KBL		IWW		
	Autumn 2015	Spring 2016	Winter 2021	Autumn 2015	Spring 2016	Winter 2021	Autumn 2015	Spring 2016	Winter 2021	Autumn 2015	Winter 2021	Spring 2016	Winter 2021	Autumn 2015	Spring 2016	Winter 2021
Temperature/ °C	10.3	9.8	11.0	11.6	12.0	10.6	13.6	13.4	9.0	12.4	7.0	14.1	8.0	11.5	19.1	-
pH	7.53	8.25	7.29	7.82	8.09	7.77	7.57	8.04	7.91	8.09	7.29	8.19	8.09	7.11	7.31	7.23
Conductivity/ µS cm^{-1}	392	378	431	526	401	497	843	283	558	1011	759	584	526	469	573	3670
TDS/mg L^{-1}	195.9	181.2	215.0	263.0	201.0	248.0	422.0	135.2	279.0	505.0	379.0	283.0	263.0	235.0	280.0	1834
ORP/mV	-19.7	-27.7	-8.2	-36.0	-51.2	-34.4	-21.8	-	-42.5	-51.2	-53.2	-	-52.0	4.1	-	-5.6
Dissolved oxygen/mg O_2 L^{-1}	10.54	10.76	10.07	10.31	12.07	10.63	8.81	11.40	10.44	10.88	11.40	10.84	12.59	4.68	5.53	-
Saturated oxygen/%	95.8	97.2	93.9	96.4	114.3	95.6	80.1	111.6	92.9	103.5	96.4	107.4	108.4	44.0	66.0	-
Nitrate/mg N L^{-1}	0.1	*0.73*	0.03	0.2	*1.20*	0.14	*2.7*	*3.7*	0.10	*1.8*	0.10	0.6	0.02	*7.3*	0.57	*9.05*
Nitrite/mg N L^{-1}	0.004	0.0104	0.01	0.10	0.0824	0.027	0.842	0.348	0.014	0.008	0.016	0.0296	0.017	0.440	0.02	7.41
Total nitrogen/mg N L^{-1}	0.4	-	0.2	0.7	-	*1.3*	*11.4*	-	1.0	*2.3*	0.9	-	0.3	*9.1*	-	*30.6*
Ammonium/mg N L^{-1}	<0.01	-	<0.01	*0.1*	-	*0.15*	*0.30*	-	0.04	*0.15*	0.02	-	<0.01	*0.45*	-	*13.15*
o-phosphate/ mg P L^{-1}	<0.01	0.035	-	<0.01	0.045	-	*0.11*	*0.18*	-	0.01	-	*0.073*	-	*0.98*	*0.069*	-
Total phosphorus/ mg P L^{-1}	<0.01	-	0.006	*0.1*	-	*0.107*	*1.03*	-	0.022	*0.2*	0.014	-	0.002	*1.96*	-	*1.35*
Turbidity/FAU	0	-	0	2	-	10	2	-	9	1	4	-	1	11	-	31
Total hardness/°dH	11.83	11.16	13.06	11.31	12.36	12.45	11.12	12.06	10.75	10.97	12.0	11.56	13.15	12.62	12.26	8.07

Metal trends



- the highest metal concentrations in TOR (Orašnica River)
- increase in metal concentrations observed in KRK and TBU compared to KRS
- similar trends in all samplings, but decline in metal concentrations is observed over the years – the highest concentrations in autumn 2015
- Ag, Sn, Pb, Bi, Ti were mostly < LOD

IWW	Li	Se	Rb	Mo	Sb	Mn	Fe	Co	Ni	Zn	As	Na	Ca	K
						μg L^{-1}							mg L^{-1}	
Autumn 2015	2.73	3.72	4.70	3.74	0.21	*598.5*	*17820*	188.693	35.17	*8503*	0.46	261.3	174.7	30.46
Spring 2016	1.84	9.31	2.47	1.76	0.35	*432.1*	*4300*	651.406	24.43	*16095*	0.26	141.8	121.8	22.32
Winter 2021	7.30	2.39	4.29	12.52	0.33	*177.5*	*75.9*	8.558	2.71	*84.2*	0.25	89.4	491.1	76.10

- **TOR** represents the most serious **threat** to Krka River watercourse directly
- **IWW** which sometimes spill to TOR have **up to 300 times higher levels** of some metals – the **highest** increase observed in **Fe, Mn** and **Zn** concentrations → used in that kind of industry!
-**Increase** of all elements seen in anthropogenically affected locations when compared with KRS

- IWW>TOR>KRK≥TBU>KBL>KRS
- Lower increase and concentrations in 2021 as a result of more efficient wastewater treatment of the basins

Conclusions

- Poorer values of many physico-chemical parameters were recorded at TOR, TBU and KRK compared to KRS ⟶ often characterized as water below good quality!

- At the affected sites, the highest increase was observed for Co, Fe, Mn, Ni and Zn, metals used in industry, but also for K, Mo, Se and Sb at IWW, TOR and TBU compared to KRS.

- Long-term research indicated mostly comparable trends, although metal levels slightly declined in the Krka River and its tributaries over the years, as a result of more efficient wastewater treatment.

- All seasons will be compared within BIOTOXMET project!

- **Increase in metal concentrations in all sites located downstream of the wastewater discharges, as well as ecological disturbances of physico-chemical parameters indicate potential danger for this sensitive karst ecosystem and the importance of regular monitoring and protection of the Krka NP.**

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