Total and dissolved metal/metalloid concentrations in water of the Krka River, its tributaries and nearby wastewaters

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Zagreb,
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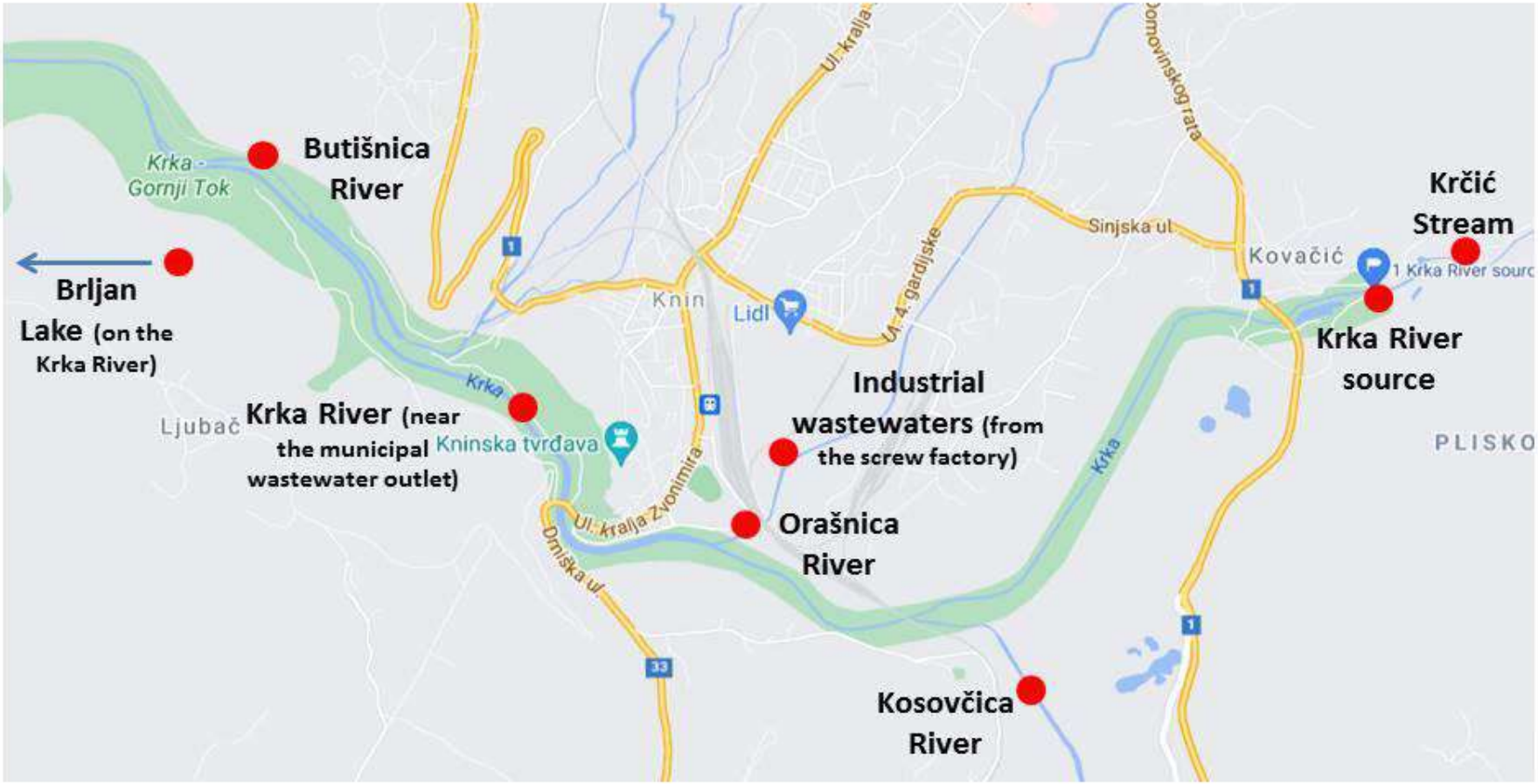
Locations:

- ✓1 Tributary Krčić – TKR
- ✓2 Krka River source – KRS
- ✓3 Kosovčica River - TKO
- ✓4 Orašnica River – TOR
- ✓5 Industrial wastewaters - IWW
- ✓6 Town of Knin – KRK
- ✓7 Butišnica River – TBU
- ✓8 Brljan Lake – KBL

Samplings:

- ✓ Winter
- ✓ Spring
- ✓ Summer
- ✓ Autumn



Procedure:

Sampling in triplicates

Field

Filtration of 20 mL

20 mL taken in the bottle

Dissolved metals

Total metals

Acidification with HNO_3 (400 µL to 20 mL)

+4 ºC

Laboratory

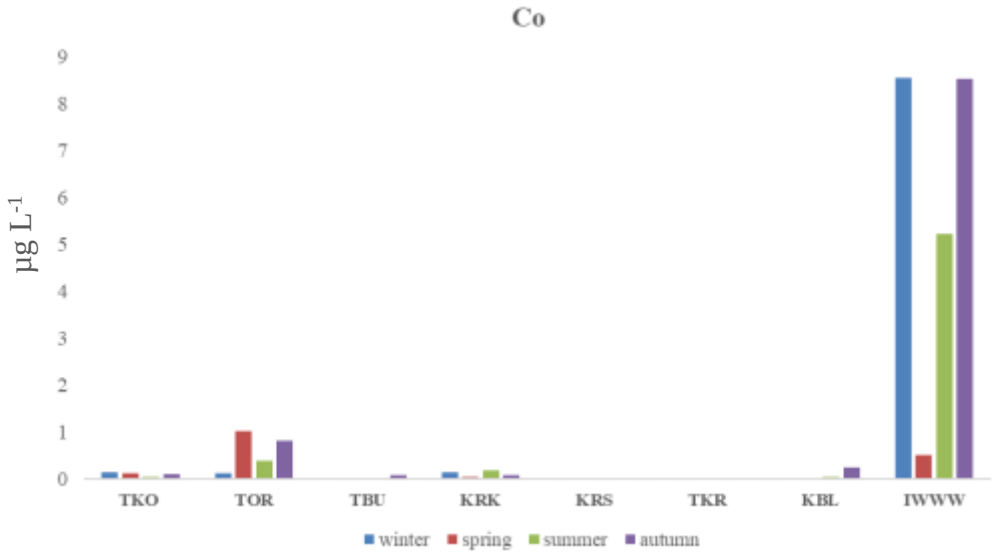
HR ICP-MS measurement

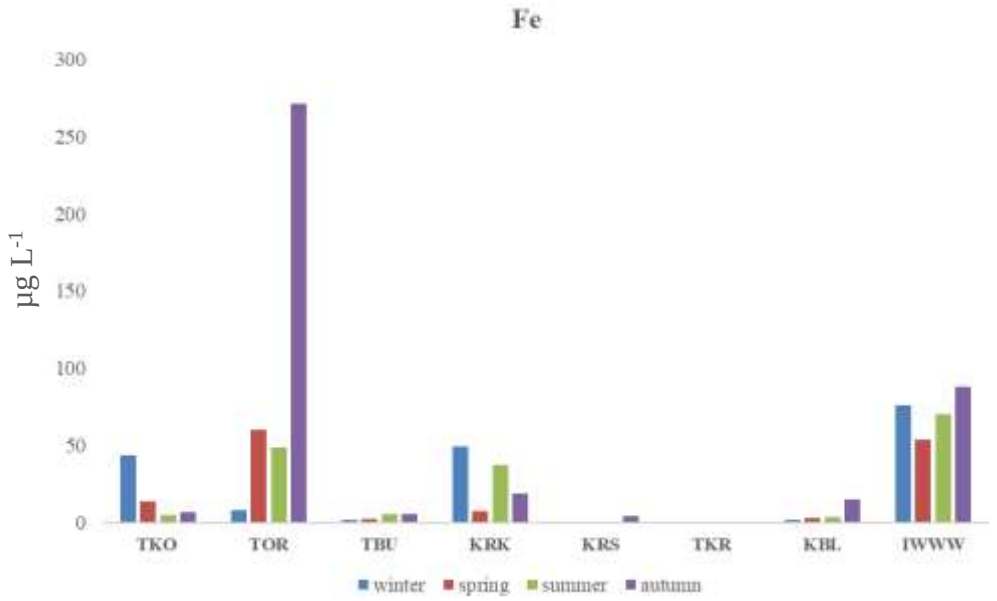
Trace elements measured directly in water samples

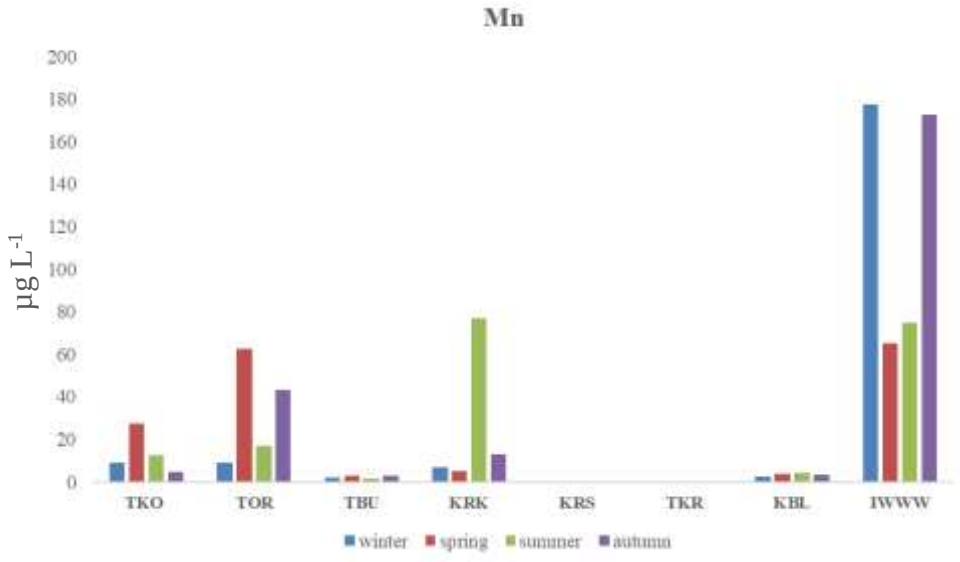
Macroelements measured in 10 times diluted water samples

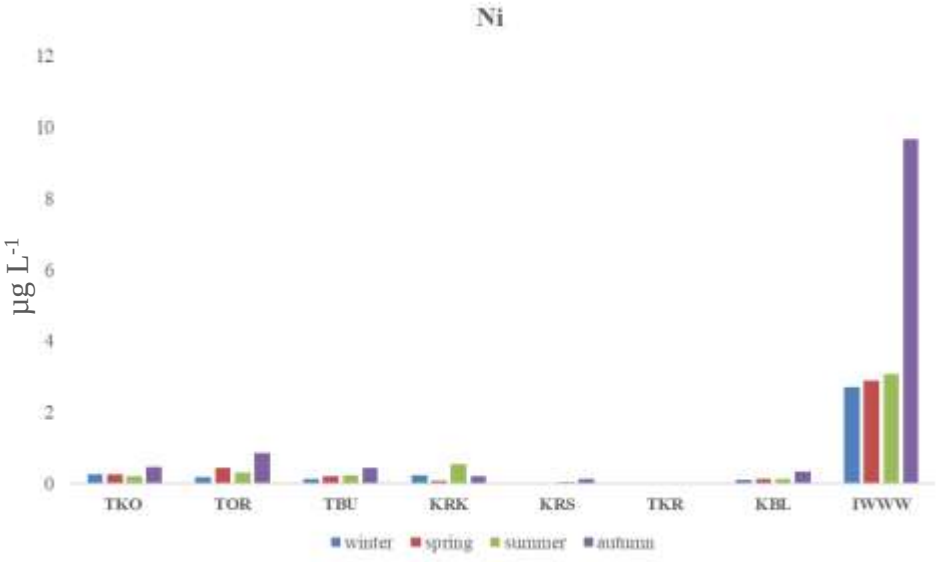
Sample preparation for ICP- MS measurement

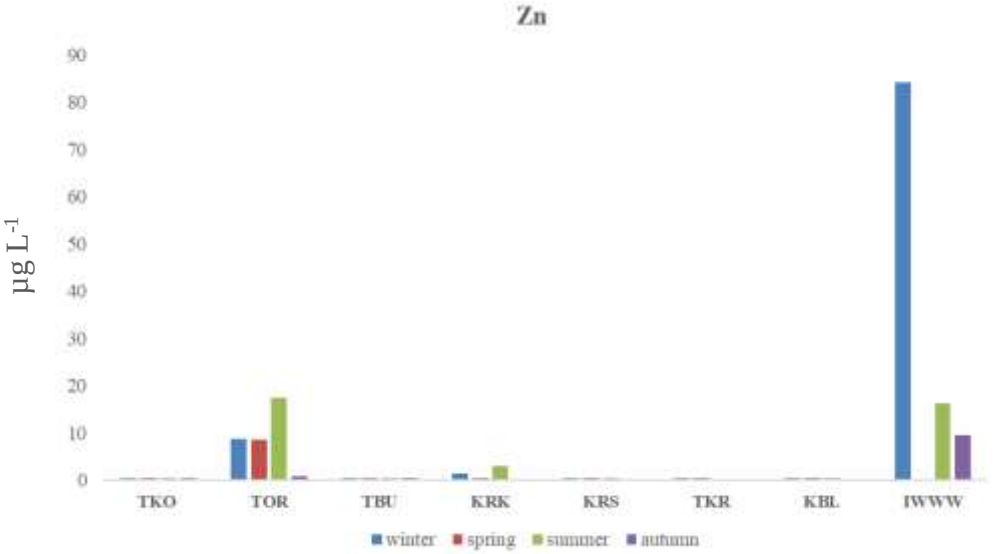
- **At the anthropogenically affected sites, the highest increase in all seasons was observed for Co, Fe, Mn, Ni and Zn, metals used in industry -** confirmed potential **impact** of **IWW** to **the Krka River** and its **tributaries**






Mn
µg L-1
200
180
160
140
120
100
80
60
40
20
0
TKO
TOR
TBU
KRK
KRS
TKR
KBL
IWWW
winter
spring
summer
autumn


Ni
µg L-1
12
10
8
6
4
2
0
TKO
TOR
TBU
KRK
KRS
TKR
KBL
IWWW
winter
spring
summer
autumn


Zn
µg L-1
90
80
70
60
50
40
30
20
10
0
TKO
TOR
TBU
KRK
KRS
TKR
KBL
IWWW
winter
spring
summer
autumn

	Mn	Fe	Co	Ni	Zn
IWW/TOR					
winter	19,77	9,55	70,42	15,01	9,57
spring	1,04	0,89	0,51	6,53	
summer	4,45	1,44	13,73	9,86	0,93
autumn	4,01	0,32	10,56	11,27	44,83
IWW/KRK					
winter	26,40	1,54	61,33	10,95	58,61
spring	13,23	7,26	17,89	36,45	
summer	0,97	1,89	29,54	5,73	5,24
autumn	13,39	4,72	106,83	43,31	333,30
IWW/TKO					
winter	19,71	1,74	65,56	10,02	162,21
spring	2,39	3,93	4,49	11,19	
summer	6,02	14,99	160,71	14,59	31,61
autumn	36,62	12,82	86,32	20,73	635,35
IWW/KRS					
winter	13654,48	1039,41	897,71	100,25	162,21
spring	5001,21	738,01	90,41	75,71	
summer	835,00	670,12	730,49	63,33	31,61
autumn	3079,68	20,33	371,57	79,82	605,33
TOR/KRK					
winter	1,34	0,16	0,87	0,73	6,12
spring	12,75	8,13	35,21	5,58	16,60
summer	0,22	1,31	2,15	0,58	5,61
autumn	3,34	14,53	10,11	3,84	7,43
TOR/KRS					
winter	690,66	108,87	12,75	6,68	16,95
spring	4820,07	826,51	177,92	11,60	16,60
summer	187,69	465,63	53,21	6,42	33,84
autumn	768,39	62,59	35,17	7,08	13,50
KRK/KRS					
winter	517,17	675,57	14,64	9,15	2,77
spring	378,15	101,67	5,05	2,08	
summer	862,81	355,21	24,73	11,05	6,03
autumn	229,96	4,31	3,48	1,84	1,82

- **IWW** which sometimes spill to TOR have **up to 70 times higher levels** of some metals – the **highest** increase observed in **Fe, Mn** and **Zn**
- **IWW** have up to **13500 times higher levels of Mn, 1000 times higher levels of Fe, 900 times higher levels of Co, 600 times higher levels of Zn and 100 times higher levels of Ni** compared to **KRS.**
- **TOR** represents the most serious **threat** to Krka River watercourse directly

- **Increase of Al, As, Ba, K, Mo, Sb, Sr and U was also evident at IWW, KRK and TOR compared to KRS and TKR**
- **Except in IWW, Ag, Sn, Pb, Hg, Bi, Ti were mostly < LOD**
- **Total and dissolved concentrations showed comparable variations**
- **Seasonal patterns were not clear and the same in all locations**

IWW>TOR>KRK≥TKO>TBU>KBL>TKR ≥ KRS

Conclusions:

- At the **affected sites**, the **highest increase** compared to KRS and TKR was observed for **Fe**, **Mn**, **Ni**, **Co and Zn** (metals used in industry)

- **Tributary Orašnica** (near IWW) was shown as the **biggest direct threat** to the pollution of Krka River → IWW basins sometimes spill to Orašnica at high water levels

- Presented results indicated the **influence** of **direct pollution sources (municipal and industrial wastewaters)**

- Increase in metal concentrations in all sites located downstream of the wastewater discharges and ecological disturbances of physico-chemical parameters indicate potential danger for this sensitive karst ecosystem ⇨ **proper purification** of the wastewaters and implementation of **regular water quality monitoring strategies** of the Krka River are required

BIOTOXMET

HrZZ
Croatian Science Foundation

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