An integrated study of metals behaviour in low Ebro River

Roig N.[1,2,*], Kılıçoğlu Ö.[1], Sierra J.[1,3], Nadal M.[2], Schuhmacher M.[1,2], Domingo JL.[2]

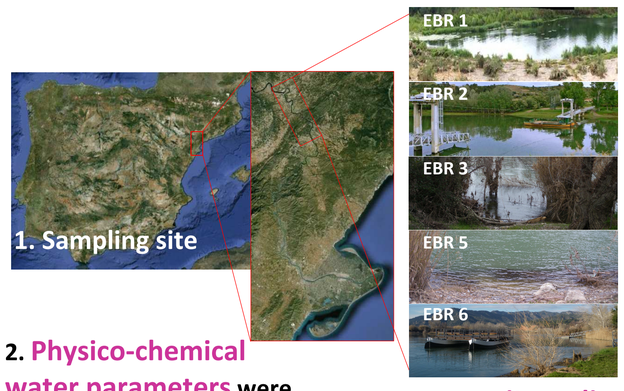
[1]Environmental Engineering Laboratory, Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Catalonia, Spain
[2]Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain
[3]Laboratori d'Edafologia, Facultat de Farmàcia, Universitat de Barcelona, Av. Joan XXIII s/n, 08028, Barcelona, Catalonia, Spain
neus.roig@urv.cat

Introduction

Metals are good indicators of anthropogenic pollution of aquatic ecosystems. They have the capability to be present in water and can be accumulated for years in sediments, being a potential sink and source of contaminants to the water column. Although most of the legislation is referred to the total concentrations of contaminants in freshwater environment, the real risk for the organisms is more related to the bioavailable fractions. However, it is still a very controversy subject.

The **Objectives** of the present study are to (I) assess the bioavailability of some potentially inorganic toxic elements in sediments of the low Ebre river (NE Catalonia, Spain), and (II) evaluate the relationship between stream metal concentrations, sediments ecotoxicity and the structure of the macroinvertebrate community.

Materials & methods



2. Physico-chemical water parameters were analyzed in situ by using a multiparametric analyzer

3. A **composite sediment sample** was prepared by mixing 5 sub-samples collected at 0–5 cm depth

4. Metal analyses of sediments

✓ **Total metal concentration**: acid digestion with HNO_3 and quantification by ICP-OES (Mn, Ni, Zn), ICP-MS (Cd, Cr, Hg, Pb) and hybride generation ICP-MS (As). (Ocampo-Duque et al., 2008)

✓ **Sequential extraction** according to the Community Bureau of Reference (BCR) method (Mossop & Davidson, 2002) : acetic acid → hydroxylammonium Cl^- → hydrogen peroxide/ammonium acetate → *aqua reggia)*

✓ **SEM/AVS Method** (*Simultaneously extracted metals (SEM) and Acid-volatile sulfide (AVS)*) *(Allen et al., 1993)*

5. Ecotoxicity

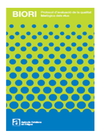
MICROTOX
Vibrio fischeri
ISO 11348-1:2007

DAPHTOXKIT F MAGNA
Daphnia magna
OECD 202

Pore water: obtained by vacuum filtration at 0.47 µm	EC50 (luminescence decrease)	EC50 (24h-48h mortality)
Organic extract: extraction according to USEPA 3546 Method (solvent evaporated and exchanged with DMSO)	EC50 (luminescence decrease)	EC50 (24h-48h mortality)
Whole sediment	EC50 (luminescence decrease)	% survival

6. Biological quality according to macroinvertebrates communities

IBMWP methodology (Alba et al. 2002), macroinvertebrates richenss and EPT index.



Results & discussion

Physical chemical parameters of water

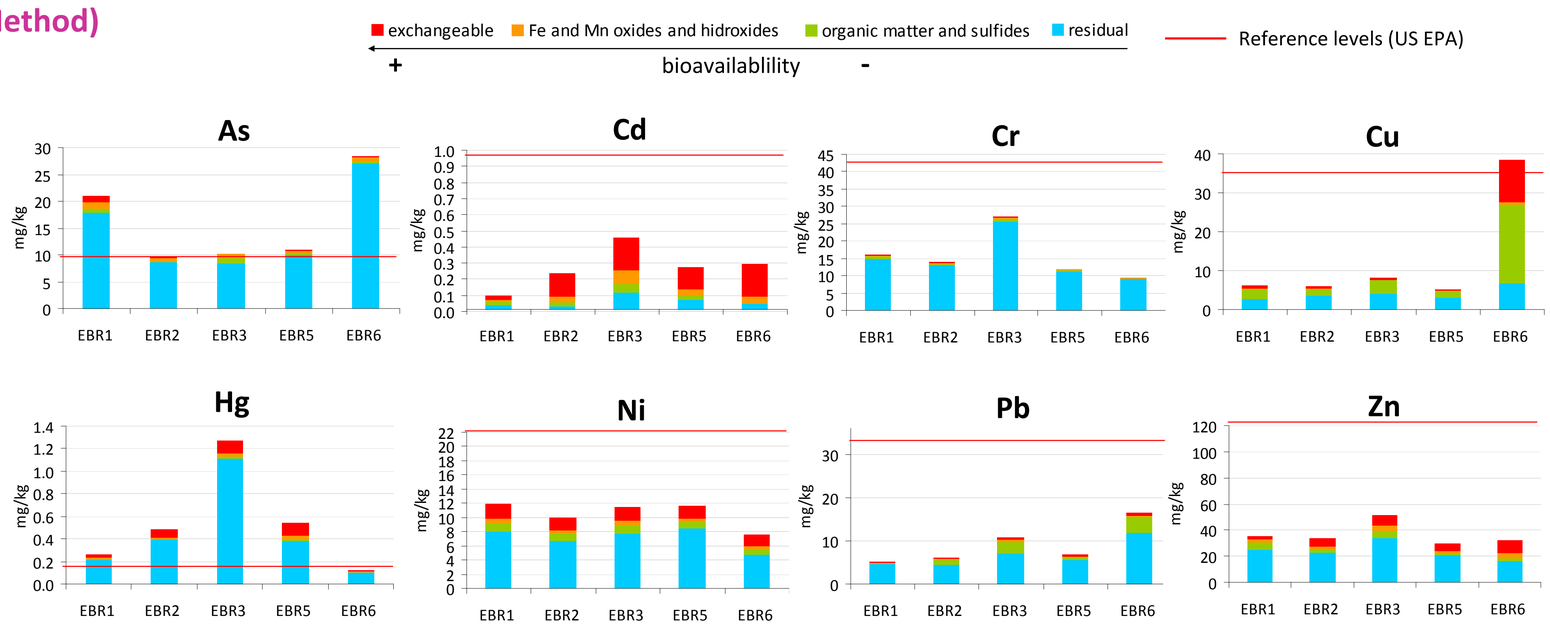
	pH	EC (dS/m)	Turbidity (NTU)	DO (mg/L)
EBR1	7.6 ± 0.7	1.2 ± 0.4	3.3 ± 0.5	9.6 ± 3.0
EBR2	8.2 ± 0.4	0.8 ± 0.2	5.0 ± 1.8	10.2 ± 1.8
EBR3	8.6 ± 1.7	1.2 ± 0.5	5.6 ± 1.5	9.3 ± 4.0
EBR5	9.0 ± 1.5	1.2 ± 0.5	7.8 ± 4.3	9.0 ± 2.3
EBR6	8.0 ± 0.2	1.2 ± 0.5	2.4 ± 0.8	9.4 ± 3.2

Ebre River **waters** are mineralized, alkaline, with low suspended solids and well oxygenated.

Metal concentration (BCR Method)

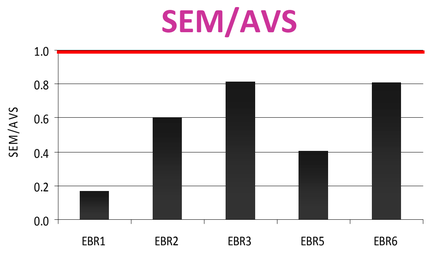
- ✓ As, Hg & Cu: exceed the reference levels in in some samples.
- ✓ Cd: high bioavailability but below benchmarks.
- ✓ Ni & Cu: available and bound to sediment organic matter.
- ✓ Cr & Pb: very low bioavailability.

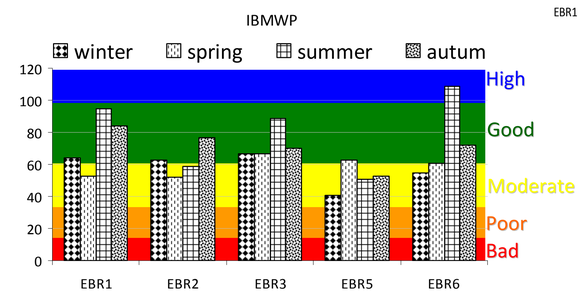
- ✓ EBR 3 presented the highest concentration of Cd, Cr, Hg & Zn.
- ✓ EBR 6 presented the highest concentration of As, Cu & Pb.

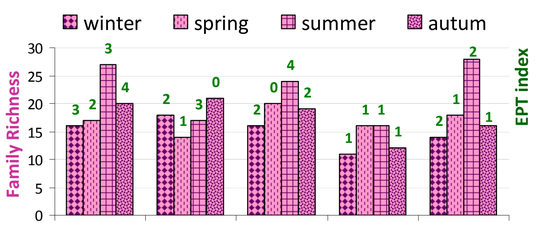


SEM/AVS

- ✓ **SEM-AVS** ratio it's below 1 in all cases, so no toxicity is expected due to cationic metals.







Biological quality

- ✓ EBR 3 presented good biological quality in all campaigns while EBR 5 presented the worst biological quality.
- ✓ The number of macroinvertebrates families ranged between 10 in winter and around 25 in summer.
- ✓ EBR 1 presented more sensitive families in most of the campaigns.

TOXICITY RANGES

Non toxic
Marginally toxic
Moderately toxic
Highly toxic

Adapted from Bombardier and Bermingham, 1999.

Ecotoxicity Tests

- ✓ Whole sediment analysis seems to be more sensitive to toxicity than pore waters, although fine texturized materials may interfere.
- ✓ Lipophilic pollutants could be more responsible to the toxicity than hydrophilic ones.
- ✓ EBR1 sediments seem to be the most ecotoxic samples for *V. fishceri*.

- ✓ Whole sediment analysis allows knowing the toxicity of lipophilic and hydrophilic pollutants at the same time.
- ✓ EBR1 sediments seem to be the most ecotoxic samples for *D. magna*.

- ***Vibrio fischeri***

	Pore water (% v/v)	Organic extracts (µL/ml)	Whole sediment (mg/L)
EBR1	57.4	1.92	906
EBR2	non effect	9.72	2586
EBR3	non effect	0.81	4414
EBR5	non effect	20.1	2996
EBR6	non effect	23.6	793

- ***Daphnia magna***

	Pore water		Organic extracts		Whole sediment	
	$EC50_{24h}$ (%v/v)	$EC50_{48h}$ (%v/v)	$EC50_{24h}$ (µL/mL)	$EC50_{48h}$ (µL/mL)	% $survival_{24h}$	% $survival_{48h}$
EBR1	10.9	8.6	34.1	17.1	0	0
EBR2	non effect	non effect	non effect	non effect	100	100
EBR3	non effect	non effect	13.5	6.8	80	20
EBR5	non effect	non effect	8.1	4.0	80	40
EBR6	non effect	non effect	non effect	non effect	80	80

Pearson Correlation

	Pore water ecotoxicity		Organic extracts ecotoxicity		Whole sediment ecotoxicity	
	V. fischeri	*D.magna*	*V. fischeri*	*D.magna*	*V. fischeri*	*D.magna*
total As					-.850	
total Ni				-.859		
available As	-.998	-.998				-.979
available Cr	-.975	-.975				-.923
available Ni	-.817	-.817	-.899			
organic mat Cr			-.848			
organic mat Ni			-.992			
organic mat Zn			-.810			
AVS	-.817	-.993				-.969

- ✓ Available metal forms tend to correlate better with toxicity than total metal concentrations.
- ✓ None significant correlation was found between biological indices and metals concentration, physico-chemical parameters or toxicity. Biological quality depends on many other factors (hydromorphology, climate, nutrients availability, water content…) than pollutants load.
- ✓ Sulfides (AVS) could be toxic for both tested organisms.
- ✓ Whole sediment test with *D.magna* correlates positively with pore water and organic extract tests.

Conclusions

- ✓ As & Cr, which form anionic spices, could be in part, the responsible of sediment toxicity to *Vibrio* & *Daphnia sp*. Specially in EBR 1 sediments which presented high As levels and also toxicity to both organisms tested.
- ✓ Cr, Ni & Zn organometals could be, among with other lipophilic pollutant, the responsible of organic extracts toxicity, specially in EBR 3 sediments that presented moderate and marginally toxicity to *V.fischeri* and *D.magna* respectively .
- ✓ Despite that sulfides (AVS) reduce the bioavailability of cationic metals, these could be the responsible, in addition to As & Cr, of sediment toxicity to *Vibrio fischeri* and *Daphnia magna.*

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Acknowledgements

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